EXHIBIT R

US005803833A

United States Patent [19]

Nakamura et al.

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[45] Date of Patent: Sep. 8, 1998

[54] TWO-PIECE SOLID GOLF BALL

[75] Inventors: Atsushi Nakamura; Hisashi Yamagishi, both of Chichibu, Japan

[73] Assignee: Bridgestone Sports Co., Ltd., Tokyo, Japan

[21] Appl. No.: 797,609

[22] Filed: Feb. 7, 1997

[30] Foreign Application Priority Data

Feb. 7, 1996 [JP] Japan 8-045444

[51] Int. Cl.⁶ A63B 37/06; A63B 37/12
[52] U.S. Cl. 473/377; 473/378; 273/DIG. 20
[58] Field of Search 473/377, 378; 273/DIG. 20

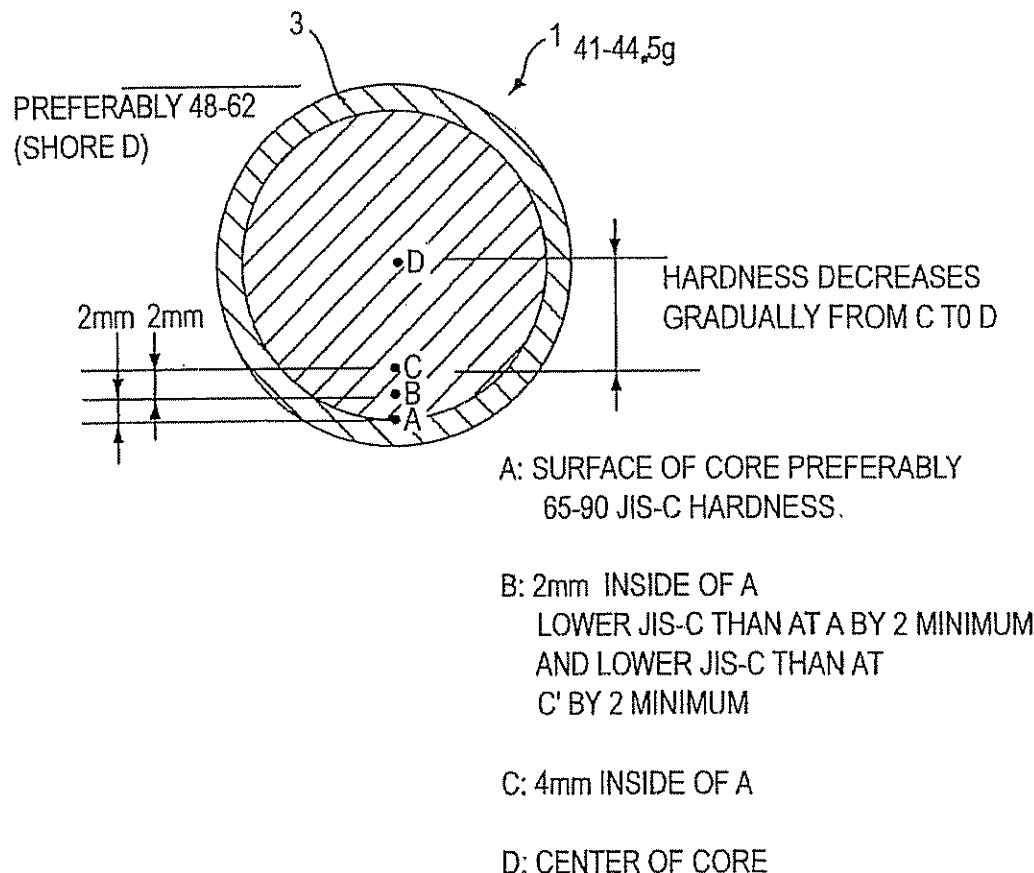[56] References Cited

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Primary Examiner—George J. Marlo
Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

[57] ABSTRACT

A two-piece solid golf ball comprising a solid core and a cover has a weight of 41–44.5 grams. The solid core has such a distribution of hardness as measured by a JIS-C scale hardness meter that the hardness at 2 mm inside the core surface is at least 2° lower than the hardness at the core surface and the hardness at 4 mm inside the core surface and the hardness gradually decreases from 4 mm inside the core surface to the core center. The ball offers all-around performance satisfying trajectory, carry, feeling, durability and spin to those players who are short in hitting the ball high and far despite a relatively high head speed.
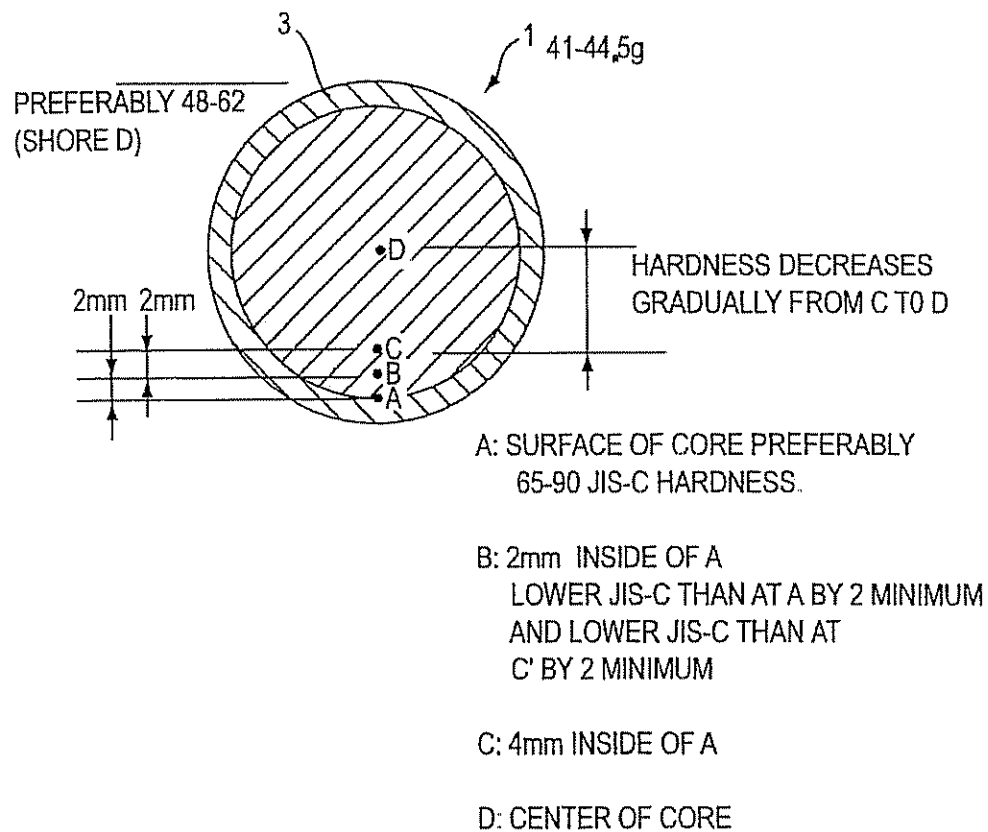
3 Claims, 1 Drawing Sheet

PREFERABLY 48-62 (SHORE D)

41-44.5g

2mm 2mm

HARDNESS DECREASES GRADUALLY FROM C TO D

A: SURFACE OF CORE PREFERABLY 65-90 JIS-C HARDNESS.

B: 2mm INSIDE OF A
LOWER JIS-C THAN AT A BY 2 MINIMUM
AND LOWER JIS-C THAN AT
C' BY 2 MINIMUM

C: 4mm INSIDE OF A

D: CENTER OF CORE

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FIG. 1

PREFERABLY 48-62
(SHORE D)

1 41-44,5g

HARDNESS DECREASES
GRADUALLY FROM C T0 D

2mm 2mm

A: SURFACE OF CORE PREFERABLY
    65-90 JIS-C HARDNESS.

B: 2mm INSIDE OF A
    LOWER JIS-C THAN AT A BY 2 MINIMUM
    AND LOWER JIS-C THAN AT
    C' BY 2 MINIMUM

C: 4mm INSIDE OF A

D: CENTER OF CORE

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TWO-PIECE SOLID GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a two-piece solid golf ball.

2. Prior Art

As the number of golf players increases in these years, the demand for golf balls with respect to their playability factors such as flight, feeling, durability and spin is diversified so as to meet the level of individual players including professional, low-handicap, average, and novice players. Nevertheless, most of advanced golf balls currently available are constructed with a focus on low-handicap players who swing at a high head speed.

Under such circumstances, those golf players who are slow in head speed, including beginner, female and senior players cannot take full advantages of the advanced balls including increased carry and pleasant feel. The reason is that the flight performance is more dependent on a head speed since a weaker force applied to the ball upon impact causes a smaller deformation to the ball.

The advanced balls are also unsatisfactory to those players who swing at a relatively high head speed, but fail to gain a long distance because of low trajectory upon shots with a driver or long iron.

Lightweight golf balls have been proposed in various versions. Such lightweight golf balls are mainly targeted for low-head speed players. Japanese Patent Application Kokai (JP-A) No. 109971/1992 proposes to impart a hardness distribution to the core at no sacrifice of feeling and durability. The ball is improved in feeling by providing a core hardness distribution determined with stress concentration taken into account while restitution is maintained. The ball is not yet adequate to those players who swing at a relatively high head speed, but fail to gain a long distance because of low trajectory.

SUMMARY OF THE INVENTION

Therefore, an object of the invention is to provide a two-piece solid golf ball which offers all-around performance satisfying such playability factors as trajectory, carry, feeling, durability and spin to those players who swing at a relatively high head speed, but fail to hit the ball high and far with a driver or long iron.

We have found that the above object can be attained by controlling the weight and core hardness distribution of a two-piece solid golf ball. (1) The ball should have a weight of 41 to 44.5 grams, which is lighter than ordinary golf balls. (2) With stress concentration taken into account, the hardness distribution of the core is adjusted such that the hardness at 2 mm inside the core surface is at least 2° lower than the hardness at the core surface and the hardness at 4 mm inside the core surface, and the hardness gradually decreases from 4 mm inside the core surface to the core center. Note that the hardness is as measured by a JIS-C scale hardness meter. Then the ball will follow a higher trajectory and gain a higher initial velocity on actual shots, traveling a longer distance. The hardness distribution of the core ensures a more pleasant feel while maintaining high restitution. If the core is formed relatively soft, then the ball presents a very soft feel. If the core is formed relatively hard, then the ball presents a pleasant feel. Consequently, if the core is formed relatively hard with the target placed on those players who can swing at a relatively high head speed, but suffer from a relatively low trajectory and a less satisfactory

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flight distance upon shots with a driver or long iron, the ball enables high trajectory shots with a pleasant feel. The ball is further improved in spin, feel and durability particularly when the cover has a hardness in the range of 48 to 62 on Shore D hardness scale. The present invention is predicated on these findings.

Accordingly, the present invention provides a two-piece solid golf ball comprising a solid core having a spherical surface and a cover enclosing the core, wherein the golf ball has a weight of 41 to 44.5 grams, and the solid core has such a distribution of hardness as measured by a JIS-C scale hardness meter that the hardness at 2 mm inside the core surface is at least 2° lower than the hardness at the core surface and the hardness at 4 mm inside the core surface and the hardness gradually decreases from 4 mm inside the core surface to the core center. Preferably the solid core has a hardness of 65° to 90° at the surface as measured by a JIS-C hardness meter. Also preferably the cover has a Shore D hardness of 48 to 62.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the golf ball of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a 2-piece solid golf ball comprising a spherical solid core and a concentric cover. According to the invention, the ball is lightweight, that is, has a weight of 41 to 44.5 grams, preferably 42 to 44 grams. If the ball weight is less than 41 grams, the ball is too light to travel a long distance. Balls having a weight of more than 44.5 grams have no significant difference from conventional solid golf balls and fail to attain the objects of the invention.

In addition to the weight requirement, the 2-piece solid golf ball of the invention requires that the hardness distribution of the core be optimized in consideration of stress concentration. When the solid core is measured for hardness by a JIS-C scale hardness meter, the core has a hardness on its spherical surface (to be referred to as surface hardness, hereinafter), a hardness at a position located 2 mm inside the surface in a radial direction, a hardness at a position located 4 mm inside the surface in a radial direction, and a hardness at the center (to be referred to as center hardness, hereinafter). The surface hardness is an average of five measurements at arbitrary five points on the core surface.

The surface hardness should preferably be 65° to 90°, more preferably 70° to 87°, most preferably 78° to 85°. If the surface hardness of the core is less than 65°, then the core would be too soft to travel a long distance. If the surface hardness of the core is more than 90°, then the core would be too hard to present a pleasant feel.

The hardness at 2 mm inside the core surface should be at least 2°, preferably at least 5° lower than the surface hardness and the hardness at 4 mm inside the core surface. The hardness at 2 mm inside the core surface should preferably be at least 60°, more preferably at least 65° in order to avoid a loss of restitution.

Preferably the hardness at 4 mm inside the core surface should be 0° to 2° lower than the surface hardness. The hardness at 4 mm inside the core surface is approximately equal to the surface hardness and preferably ranges from 65° to 88°, especially 68° to 85°.

Further the hardness should gradually decrease from 4 mm inside the core surface to the core center. The center hardness is preferably 50° to 70°, especially 50° to 60°.

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A solid core having the above-defined hardness distribution may be formed by blending a base rubber with a mixture of dicumyl peroxide and 1,1-bis-3,3,5-trimethylcyclohexane as a crosslinking agent and vulcanizing the rubber at 160° C. for 20 minutes.

The solid core as a whole should preferably have a distortion of 1.8 to 5.0 mm, especially 3.0 to 4.7 mm under a load of 100 kg. Although the diameter, weight and specific gravity are not critical, the solid core preferably has a diameter of 37.0 to 41.0 mm, especially 38.0 to 40.0 mm and a weight of 27.0 to 40.0 grams, especially 30.0 to 37.0 grams.

The solid core may be formed from conventional solid core stock materials by conventional methods while formulation and vulcanizing conditions are adjusted so as to meet the core requirement of the invention. Most often, the core is formed of a composition comprising a base rubber, a crosslinking agent, a co-crosslinking agent, and an inert filler as used in the formation of conventional solid cores. The base rubber used herein may be natural rubber and/or synthetic rubber conventionally used in solid golf balls although 1,4-polybutadiene having at least 40% of cis-structure is especially preferred in the invention. The polybutadiene may be blended with a suitable amount of natural rubber, polyisoprene rubber, styrene-butadiene rubber or the like if desired. The crosslinking agent is typically selected from organic peroxides such as dicumyl peroxide, di-t-butyl peroxide, and 1,1-bis-3,3,5-trimethylcyclohexane, with a mixture of dicumyl peroxide and 1,1-bis-3,3,5-trimethylcyclohexane being preferred. About 0.5 to 3 parts by weight of the crosslinking agent is generally blended with 100 parts by weight of the base rubber. The co-crosslinking agent is typically selected from metal salts of unsaturated fatty acids, inter alia, zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms (e.g., acrylic acid and methacrylic acid) though not limited thereto. Zinc acrylate is especially preferred. Examples of the inert filler include zinc oxide, barium sulfate, silica, calcium carbonate, and zinc carbonate, with zinc oxide and barium sulfate being often used. The amount of the filler blended is preferably up to about 40 parts by weight per 100 parts by weight of the base rubber although the amount largely varies with the specific gravity of the core and cover, the weight of the ball, and other factors. In the practice of the invention, the amounts of the crosslinking agent and filler (typically zinc oxide and barium sulfate) are properly selected so as to provide the desired hardness and weight to the core as a whole.

A core-forming composition is prepared by kneading the above-mentioned components in a conventional mixer such as a Banbury mixer and roll mill, and it is compression or injection molded in a core mold. The molding is then heat cured as previously mentioned, so as to produce a solid core having an optimum hardness distribution.

Next, the cover enclosing the solid core should preferably have a Shore D hardness of 48 to 62, especially 50 to 60. If the Shore D hardness of the cover is less than 48, some balls would provide insufficient restitution and feeling without click. If the Shore D hardness of the cover is more than 62, there is a risk of exacerbating spin and feeling. The gage (radial thickness) of the cover is not critical although it preferably has a gage of 1.2 to 2.5 mm, especially 1.4 to 2.3 mm.

The cover is formed of any well-known cover stock, typically based on an ionomer resin. For example, Surlyn 8220 and 8120 (E. I. duPont) and Himilan 1605, 1601, 1557,

and 7315 (Mitsui duPont Polychemical K.K.) may be used alone or in admixture of two or more. Also, well-known additives such as titanium dioxide, barium sulfate, and magnesium stearate may be added to the ionomer resin for adjusting a specific gravity and hardness. UV absorbers, antioxidants and dispersing aids such as metal soaps may be added if desired. The cover stock may be molded over the solid core by any desired method, for example, by surrounding the core by a pair of preformed hemispherical cups followed by heat compression molding or by injection molding the cover stock over the core.

The thus obtained golf ball of the invention is conventionally formed with a multiplicity of dimples in the cover surface. The ball is further subject to finishing steps including buffing, painting and stamping.

While the solid golf ball of the invention is constructed as mentioned above, the diameter, initial velocity and symmetry of the ball may be properly selected in accordance with the Rules of Golf.

According to the present invention, a 2-piece solid golf ball characterized by a relatively light weight and an optimum core hardness distribution is best suited for those players who can swing at a relatively high head speed, but suffer from a relatively low trajectory and a less satisfactory flight distance upon shots with a driver or long iron, because the ball offers all-around performance satisfying trajectory, carry, feeling, durability and spin upon shots by such players.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation. All parts are by weight.

Examples 1–3 & Comparative Examples 1–2

A solid core was prepared by milling a solid core-forming rubber composition formulated as shown in Table 1 in a roll mill and vulcanizing it in a mold at 160° C. for 20 minutes in Examples 1–3 and Comparative Example 1. In Comparative Example 2, the composition was vulcanized at 120° C. for 80 minutes to produce a core having a flat hardness distribution. A cover stock formulated as shown in Table 1 was then injection molded over the solid core, obtaining 2-piece solid golf balls.

The golf balls were examined for flight performance, spin, feeling, and durability by the following tests.

Flight Test

Using a swing robot, the ball was hit with a driver (#1 W) at a head speed of 45 m/sec. (HS45) for determining a carry, total distance, and angle.

Spin

Using a swing robot, the ball was hit with a sand wedge (#SW) at a head speed of 19 m/sec. (HS19) for determining a spin rate.

Feeling Test

Five players actually hit the ball to judge the hitting feel. The rating was "⊙" for a very soft feel, "O" for a soft feel, and "Δ" for a rather hard feel.

Durability

Using a flywheel hitting machine, the ball was repeatedly hit at a head speed of 38 m/sec. until it was broken. In accordance with the count of hits, the ball was rated "⊙" for high durability, "O" for acceptable durability, and "X" for poor durability.

The results are shown in Table 1.

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TABLE 1

			E1	E2	E3	CE1	CE2
Core composition (pbw)							
Cis-1,4-polybutadiene rubber			80	85	100	90	100
Polyisoprene rubber			20	15	—	10	—
Zinc acrylate			30	30	23	27	20
Zinc oxide			6	12	12.5	25	14
Dicumyl peroxide			0.9	0.9	0.9	0.9	0.9
1,1-bis-3,3,5-trimethylcyclohexane			0.3	0.3	0.3	0.3	0.3
Cover composition (pbw)							
Surlyn 8220			—	—	—	50	—
Himilan 7315			—	—	—	50	—
Himilan 1605			50	—	—	—	—
Himilan 1557			50	50	60	—	50
Himilan 1601			—	50	—	—	50
Surlyn 8120			—	—	40	—	—
Cover hardness (Shore D)			60	58	53	68	58
Ball weight (g)			42.5	44.0	43.3	45.4	43.3
Core hardness	Surface		78	80	72	80	62
(JIS-C)	2 mm inside		73	78	66	78	62
	4 mm inside		77	80	72	80	62
	Center		65	64	56	64	48
Performance	#1W/HS45	Carry (m)	209.0	210.5	209.0	207.0	205.0
		Total (m)	217.5	219.5	218.0	216.5	212.0
		Angle (°)	12.3	12.0	12.2	11.8	12.2
	#SW/HS19	Spin (rpm)	4655	4892	5715	3860	4920
Feel			O	O	⊚	△	△
Durability			⊚	O	O	△	O

In Table 1, Surlyn and Himilan are the trade names of ionomer resin commercially available from E. I. duPont and Mitsui duPont Polychemical K.K., respectively.

As seen from Table 1, the ball of Comparative Example 1 has the same core hardness distribution as the ball of Example 2, but is different in ball weight and cover Shore D hardness. The ball of Comparative Example 1 follows a relatively low trajectory and does not travel a satisfactory distance because of the heavy weight and is inferior in spin, feel and durability because of the increased hardness of the cover. The ball of Comparative Example 2 which has a soft core and a flat core hardness distribution in that the hardness remains equal at the surface, 2 mm inside the surface and 4 mm inside the surface does not travel a satisfactory distance and presents an unpleasant feel.

In contrast, the 2-piece solid golf balls having an optimum ball weight, core hardness distribution and cover hardness within the scope of the invention exhibit all-around performance since they follow a relatively high trajectory, travel a satisfactory distance and are improved in spin, feel and durability

Japanese Patent Application No. 45444/1996 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A two-piece solid golf ball comprising a solid core having a spherical surface and a cover enclosing the core, wherein

the golf ball has a weight of 41 to 44.5 grams, and said solid core has such a distribution of hardness as measured by a JIS-C scale hardness meter that the hardness at 2 mm inside the core surface is at least 2° lower than the hardness at the core surface and the hardness at 4 mm inside the core surface and the hardness gradually decreases from 4 mm inside the core surface to the core center.

2. The golf ball of claim 1 wherein said solid core has a hardness of 65° to 90° at the surface as measured by a JIS-C scale hardness meter.

3 The golf ball of claim 1 wherein said cover has a Shore D hardness of 48 to 62

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EXHIBIT S

US005184828A

United States Patent [19]

Kim et al.

[11] Patent Number: 5,184,828

[45] Date of Patent: Feb. 9, 1993

[54] SOLID THREE-PIECE GOLF BALL

[75] Inventors: Moon K. Kim; In H. Hwang, both of Seoul, Rep. of Korea

[73] Assignee: Ilya Co. Ltd., Seoul, Rep. of Korea

[21] Appl. No.: 699,933

[22] Filed: May 14, 1991

[30] Foreign Application Priority Data

Jun. 1, 1990 [KR] Rep. of Korea 90-8095

[51] Int. Cl.⁵ A63B 37/06
[52] U.S. Cl. 273/228; 273/230
[58] Field of Search 273/220, 230, 62, 228, 273/218, 219, 225, 229

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Primary Examiner—George J. Marlo
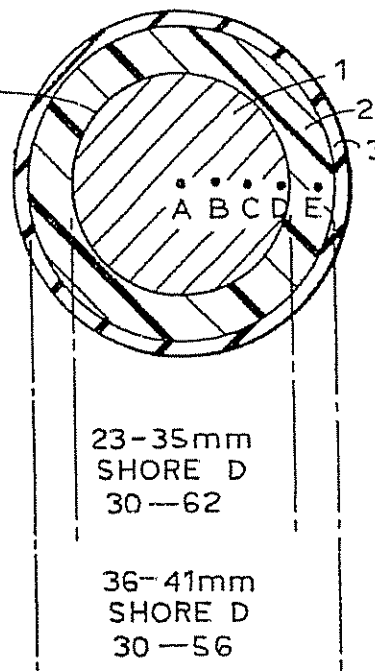Attorney, Agent, or Firm—Amster, Rothstein & Ebenstein

[57]   ABSTRACT

A non-wound three-piece golf ball which comprises an inner core, an outer layer and a cover, the inner core having a diameter of 23–35 mm and a hardness (Shore D) of 30–62, the outer layer having a diameter of 36–41 mm and a hardness (Shore D) of 30–56, the golf ball having a hardness (Shore D) 46–62 at the outer site in the inner core, which is 11.5–17.5 mm apart from the center of the ball. The golf ball has a maximum hardness (Shore D) in the range of 46–62 at the outer site of the inner core which is located at the interface between the inner core 1 and the outer layer 2 of the golf ball and the hardness then decreases both inwardly and outwardly.

5 Claims, 2 Drawing Sheets

FROM CENTER
11.5 - 17.5 ᵐ/ₘ apart   SHORE D 46–62

CENTER   A. SHORE D 30–48

5 ᵐ/ₘ apart   B. SHORE D 40–35

10 ᵐ/ₘ apart   C. SHORE D 43–58

14 ᵐ/ₘ apart   D. SHORE D 46–62

18 ᵐ/ₘ apart   E. SHORE D 30–56

23–35mm SHORE D 30—62

36–41mm SHORE D 30—56

F I G. 1

FROM CENTER
$11.5 - 17.5$ $^m/_m$ apart

SHORE D
$46 - 62$

CENTER   A. SHORE D $30-48$

$5^m/_m$ apart   B. SHORE D $40-35$

$10^m/_m$ apart C. SHORE D $43-58$

$14^m/_m$ apart D. SHORE D $46-62$

$18^m/_m$ apart E. SHORE D $30-56$

A B C D E

$23-35$mm
SHORE D
$30 - 62$

$36-41$mm
SHORE D
$30 - 56$

$24-29$m$_m$
SHORE D
$15-30$

$36-41$mm
SHORE D
$55-65$

F I G. 4
PRIOR ART

F I G. 2

SHORE D
46-62

— 1a
— 2a
— 3a
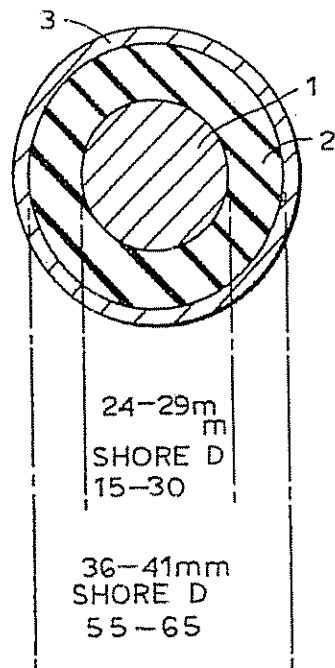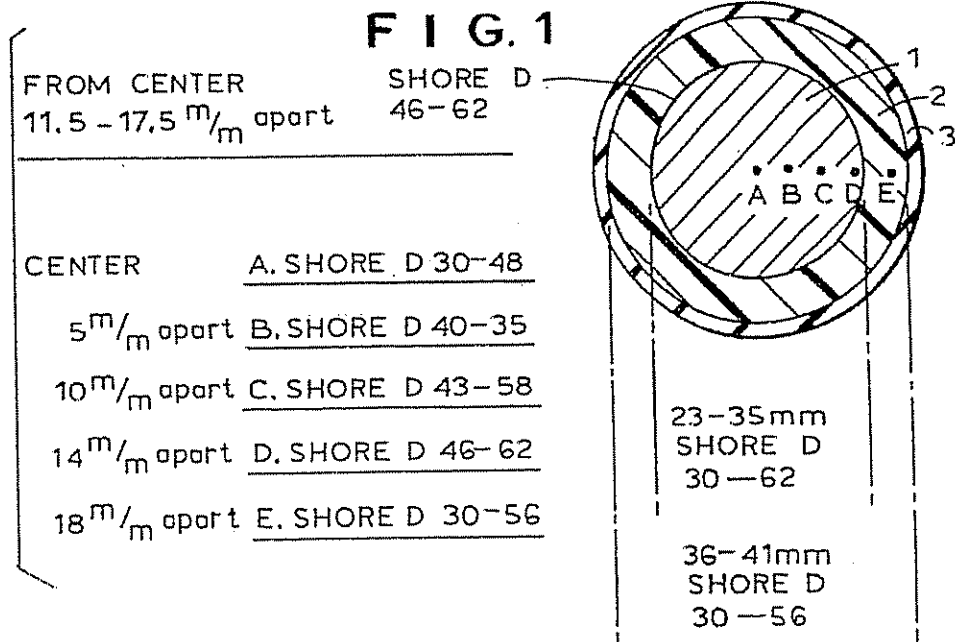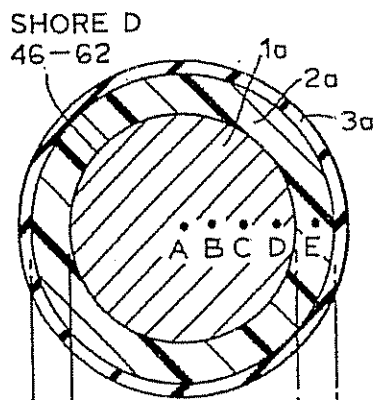
CETER   A. SHORE D 30-48

5 $^m/_m$ apart   B. SHORE D 40-35

10 $^m/_m$ apart   C. SHORE D 43-58

14 $^m/_m$ apart   D. SHORE D 46-62

18 $^m/_m$ apart   E. SHORE D 30-56

A B C D E

23-35mm
SPECIFIC
GRAVITY
1.15-1.5
SHORE D
30-62

36-41mm
SPECIFIC
GRAVITY
1.0 -1.2
SHORE D
30 - 56

F I G. 3

SHORE D
46-62

— 1b
— 2b
— 3b

A B C D E

23-35mm
SPECIFIC
GRAVITY
1.0 -1.2
SHORE D
30-62

36-41mm
SPECIFIC
GRAVITY
1.15 -1.8
SHORE D
30-56

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SOLID THREE-PIECE GOLF BALL

The present invention relates to a solid three-piece golf ball having improved rebound characteristics and carry distance while maintaining adequate spin performance. These properties are obtainable by controlling the size of the inner core and outer layer as well as the specific gravity and hardness.

The carry distance and spin performance of a golf ball are very important for the game. Although a solid two-piece ball generally has good rebound characteristics and carry distance, the core is too hard to provide a good spin performance. On the other hand, while a thread wound golf ball generally has a good spin performance, the rebound characteristics and carry distance deteriorate as the wound thread is loosened by prolonged use of the ball.

U.S. Pat. No. 4,781,383 discloses a solid three-piece ball as shown in FIG. 4, which was obtained by controlling the size and hardness of the inner core and the outer layer. This ball has a carry distance similar to that achieved by a solid two-piece ball and feels similar to a conventional thread wound ball. However, this ball has a soft inner core and a hard outer layer. Therefore, it cannot provide a satisfactory carry distance and spin performance.

The total distance achieved by a golf ball includes the carry distance and the run distance. However, the carry distance is very important since the run distance is not accurate due to the unevenness of the ground. The carry distance of a golf ball is directly influenced by its rebound characteristics. Under identical rebound characteristics and aerodynamic conditions (dimple characteristics of the ball), the lifting ability of a ball is improved if the spin rate is increased. Therefore, the peak of the trajectory gets higher, thereby providing an increase in carry distance, as the spin rate increases until the spin rate is increased up to about 2500–3000 RPM, when the ball is struck by a driver.

The present invention provides a solid three-piece golf ball having superior rebound characteristics and carry distance, while maintaining adequate spin rate. These effects are achieved by controlling the sizes, specific gravity and hardness of each part of the solid three-piece golf ball.

In accordance with the present invention there is provided a solid three-piece golf ball comprising a core assembly provided by an inner core 1 and an outer layer 2 and a cover 3 characterized by the following features:

a) the inner core 1 has a diameter in the range 23–35 mm and hardness (Shore D) in the range 30–62;

b) the outer layer 2 has a diameter in the range 36–41 mm and hardness (Shore D) in the range 30–56;

c) the golf ball has a maximum hardness (Shore D) in the range of 46–62 at the outer site of the inner core which is located at the interface between the inner core 1 and the outer layer 2 of the golf ball and the hardness then decreases towards both sides.

Referring to the drawings:

FIG. 1 is a sectional view of a solid three-piece golf ball in accordance with the present invention.

FIG. 2 is a sectional view of a first embodiment (type 1) of the golf ball according to the present invention.

FIG. 3 is a sectional view of a second embodiment (type 2) of the golf ball according to the present invention.

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FIG. 4 is a sectional view of the solid three-piece golf ball according to the U.S. Pat. No. 4,781,383.

As shown in FIG. 1, the solid three-piece ball according to the present invention comprises an inner core (1), an outer layer (2) covering the inner core and a cover (3) for protecting the outer layer.

If the surface of the inner core of the solid two-piece ball is soft, the difference between the moduli of elasticity of the inner core and the cover is increased. This generally tends to cause a reduction of rebound coefficient of the ball.

However, it has been found that the rebound characteristics of a solid three-piece golf ball can be improved by controlling the hardness distribution in the outer layer and the inner core in such a way that the golf ball has a maximum hardness at the outer site in the inner core as shown in FIG. 1, which is located at the interface between the inner core and the outer layer of the golf ball, and then the hardness decreases from that site both towards the outer surface of the outer layer and towards the center of the inner core. It has also been found that such a distribution of hardness in the core assembly allows a high energy to accumulate at the interface region where the hardness is maximum. Therefore, when the solid three-piece golf ball according to the present invention is struck by the club, the energy of the club face is efficiently delivered to the maximum hardness region and transferred toward the inner core without loss thus resulting in a high rebound coefficient. It has been observed that the fluctuation of hardness (Shore D) within 2, however, does not adversely affect the efficient transfer of the energy or spin performance of the golf ball of the present invention.

It has been found that the golf ball according to the present invention has adequate spin performance to provide an optimum trajectory resulting in an increase of carry distance since the outer layer is softer than the inner core. Furthermore, the golf ball of the present invention advantageously provides a delayed departure of the golf ball during the putting.

The diameter of the inner core of the golf ball according to the present invention is set to 23–35 mm. If the diameter of the inner core is less than 23 mm, the diameter of the soft outer layer has to be increased and rebound characteristics are adversely affected. On the other hand, if the diameter of the inner core exceeds 35 mm, the diameter of the outer layer has to be decreased, and feeling would be adversely affected due to the hard inner core.

The hardness (Shore D) of the inner core is preferably set in the range of 30–62. A inner core having a hardness (Shore D) less than 30 is too soft to give rebound characteristics necessary for reaching near the initial velocity limitation 250 ft/sec (+2% tolerance) required by U.S.G.A. and R. & A. If the hardness (Shore D) exceeds 62, the feeling of the ball is adversely affected.

The diameter of the outer layer is set to 36–41 mm. If it is less than 36 mm, the carry distance will be decreased due to the increased thickness of the cover. On the other hand, if the diameter of the outer layer is greater than 41 mm, the thickness of the cover will have to be decreased thereby adversely affecting the durability of the ball.

The hardness (Shore D) of the outer layer is set to 30–56 since if the outer layer has a hardness (Shore D) less than 30 it is too soft to provide the rebound characteristics necessary for reaching near the initial velocity

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250 ft/sec (+2% tolerance). If the hardness (Shore D) exceeds 56, it is difficult to obtain an adequate spin performance.

The hardness (Shore D) of the outer site in the inner core, which is located near the interface between the inner core and the outer layer, is set to 46–62 because, if the hardness (Shore D) is less than 46, it is not possible to accumulate a high energy, while, if the hardness (Shore D) is greater than 62, the feeling of the ball will be adversely affected.

The first embodiment (type 1) shown in FIG. 2 of the present invention has the following specification:

Inner core

Diameter (mm): 23–35
Specific gravity: 1.15–1.5
Hardness (Shore D): 30–62

Outer layer

Diameter (mm): 36–41
Specific gravity: 1.0–1.2
Hardness (Shore D): 30–56

The outer site in the inner core

Hardness (Shore D): 46–62

The solid three-piece ball of this type provides a superior carry distance even if the cover (3a) is made of hard resin since the outer layer (2a) is soft and the specific gravity of the inner core is greater than that of the outer layer, which provides an adequate spin performance, when the ball is struck by club, allowing an optimum trajectory and a superior carry distance of the ball. This type of golf ball especially provides a keen back spin when the ball is struck by a short iron.

The second embodiment of the present invention as shown in FIG. 3 has the following specification.

Inner core

Diameter (mm): 23–35
Specific gravity: 1.0–1.2
Hardness (Shore D): 30–62

Outer layer

Diameter (mm): 36–41
Specific gravity: 1.15–1.8
Hardness (Shore D): 30–56

The outer site in the inner core

Hardness (Shore D): 46–62

Generally, the carry distance is decreased if the specific gravity of the outer layer is greater than that of the inner core. However, the solid three-piece ball having the above specification provides a superior carry distance since the outer layer (2b) is soft and an adequate spin performance allows an optimum trajectory to be formed, although the cover (3b) is made of hard resin. This type of golf ball especially provides a trajectory which is less affected by the wind.

Each of the above two types of solid three-piece golf ball has its own characteristics, and a golfer may choose any type of golf ball depending on the peculiarity of his swing, such as, e.g., club head speed, ability of producing spin, and angle of launching the ball.

The inner core and the outer layer comprises a rubber base, co-cross linking agent, filler, polymerization initiator, antioxidant and the like. As a base rubber, Cis-1, 4 polybutadiene alone may be used. If necessary, natural

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rubber, isoprene rubber, and/or styrene-butadiene rubber may be optionally added to 1, 4-polybutadiene.

The co-cross linking agent comprises a compound selected from α,β-ethylenically unsaturated carboxylic acids and metal salts thereof. Trimethylol propane trimethacrylate may be optionally added. Examples of α,β-ethylenically unsaturated carboxylic acids are acrylic acid and methacrylic acid. Metal salts thereof include zinc diacrylate, zinc dimethacrylate, and the like.

The amount of co-cross linking agent used in the inner core is 35–50 parts (weight) for 100 parts (weight) of the base rubber, while the amount of co-cross linking agent used in the outer layer is 25–40 parts (weight).

Fillers which can be used include metal oxides, such as, lead oxide, iron oxide as well as barium sulfate, silica, calcium carbonate and the like. If acrylic acid or methacrylic acid is used, the preferred filler is zinc oxide. The amount of the filler is not limited although it usually depends on the specific gravity or hardness of the inner core or the outer layer to be prepared. The preferred amount of the filler is 1–50 parts (weight) and of the base rubber is 100 parts (weight).

The polymerization initiator includes an organic peroxide, such as, dicumyl peroxide, N-butyl-4, 4'-bis (t-butylperoxy) valerate, bis (t-butylperoxy isopropyl) benzene, 1-1'-bis (t-butylperoxy)-3, 3, 5-trimethyl cyclohexane. The amount of the initiator is 0.2–3.0 parts (weight) of the base rubber is 100 (weight).

If necessary, a coagent such as N-N'-m'-phenelene dimaleimide and the like may be optionally used.

An antioxidizing agent, such as, 2-2'-methylene-bis (4-methyl-6-t-butylphenol) and the like may be added. The amount is preferably 0.5–1.5 parts (weight) of 100 parts (weight) of the base rubber.

The process for preparing the inner core comprises mixing the above components by a conventional mixing apparatus, such as an internal mixer, two roll mill or the like and then subjecting the composition to compression or injection molding.

The compression or injection molding is an important step in the above process, in which the cross linking reaction by the co-cross linking agent takes place with the aid of the initiator under a given temperature and time so as to give the desired hardness distribution in the inner core.

The hardness distribution to be obtained is influenced by the co-cross linking agents and initiators as well as by the temperature and time used for curing.

For each co-cross linking agent, there is an initiator suitable for that co-cross linking agent. The amount of the cross linking agent may be minimized without adversely affecting the hardness distribution when the cross linking reaction is carried out at the reaction temperature, which is 10°–50° C. higher than the decomposition temperature of the initiator used.

If the cross linking reaction takes place at a temperature lower than the above, the distribution of hardness suitable for the present invention cannot be obtained, while, at a temperature higher than the above, a uniform distribution of hardness cannot be obtained.

If the cross linking agent is highly volatile, an initiator with a relatively low decomposition temperature may preferably be used. While the co-cross linking agent is not highly volatile, an initiator having a higher decomposition temperature may preferably be used.

If the cross linking reaction takes place at a higher temperature, the rubber molecules are broken resulting

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in remarkable degradation of physical properties of the rubber, such as, the resilience and durability of the rubber, due to severe micro Brown motion and nascent oxygen. Therefore, it is necessary to carry out the cross linking reaction with the aid of an initiator having a decomposition temperature which is 0°–50° C. lower than the boiling point of the co-cross linking agent, α,β-ethylenically unsaturated carboxylic acid.

When an initiator having a relatively low decomposition temperature is used, it is necessary to carry out the cross linking reaction at the temperature which is 20°–50° C. higher than the decomposition temperature for a relatively long time, such as, 10–40 minutes so as to obtain an optimum hardness distribution without adversely affecting other physical properties.

On the other hand, if the initiator with a relatively high decomposition temperature is employed, it is necessary to carry out the cross linking reaction at a temperature which is 10°–40° C. higher than the decomposition temperature for a relatively short period of time, such as, 5–25 minutes.

According to the present invention, the cross linking takes place and the curing of the rubber proceeds when the starting mixture is subjected to heat and pressure predetermined depending on the initiator used. When the heat is transferred through the mixture and rubber is expanded, the co-cross linking agent used is partially evaporated near the metal oxides or salts and the co-cross linking agent in gaseous form migrates from the inner part of the inner core (1) towards the outer part of the inner core carrying out the cross linking reaction of the rubber with the aid of the initiator. Therefore, the cross linking reaction is more active near the outer region of the inner core (1) than at the centre region of the inner core (1) thus resulting in a higher hardness near the outer surface than at the inner region of the core (1).

When the starting mixture is expanded by heating, the mold will be opened unless the mold is prevented from being opened by adding pressure.

Acrylic acid or methacrylic acid form a high molecular weight polymer in the form of matrix having a metal nucleus. The uniformity of cis bonding or cross linking depends on the uniformity of the starting mixture and the heat transfer.

Even after the cross linking is completed, the mixture is continuously expanded by heat until the whole process is completed. It has been found that, due to the pressure added to prevent the opening of the mold, the most dense layers are formed in the region, which is near to the cavity of the mold, namely, the outmost region of the inner core, thus resulting in a gradual increase of the hardness from the centre of the inner core towards the outer part of the inner core forming a maximum hardness site near the interface.

The molecular chains in the most dense layers of the high molecular product are compressed like springs due to the pressure caused by the expansion of the mixture. Therefore, it is possible to store a higher energy.

The outer layer (2) can be prepared by a process similar to that for the inner core (1), although the compression molding as described in the Example is preferred. However, it is important to prevent the outer surface of the outer layer from being too hard so as to obtain the desired hardness distribution as required in the present invention.

However, it is preferred that the crosslinking of the two-piece solid core assembly is carried out at a lower

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temperature than that for the crosslinking of the inner core to obtain the desired hardness distribution for the present invention.

The starting mixture for preparing the outer layer as well as the solid inner core is also expanded when it is subjected to heating. The expansion in the outer layer is greater than that in the inner core thus resulting in the most dense molecular chains being formed near the interface region between the inner surface of the outer layer and surface of the inner core.

Furthermore, a part of the cross linking agent included in the starting mixture for the outer layer evaporates and the gaseous components formed penetrate into the surface of the inner core rendering a strong binding of the outer layer with the inner core.

The resulting core assembly, which consists of the outer layer and the inner core, has such a hardness distribution that the peak of hardness appears at the outer site in the inner core, which is near the interface between the inner core and the outer layer and that the hardness is gradually decreased toward both sides.

When the ball is struck, it is presumed that the energy given by the club face is efficiently delivered and stored at the site where the hardness is the highest. Then, the energy stored is released toward the inside of the inner core without loss thus resulting in a high rebound coefficient.

The core assembly has a diameter of 36–41 mm and a hardness (Shore D) of 30–62. As mentioned earlier, two types of core assembly are available.

The core assembly is then covered with a resin having a good impact and weather resistance of 0.9–2.6 mm in thickness. The resin may contain inorganic filler, pigment and etc.

As a cover material, balata rubber or ionomer resin (such as "Surlyn" resin marketed by Du Pont Co.) or polyurethane or the like is used, although the ionomer resins are preferred.

The covering is carried out by an injection or compression molding. Finally, the cover is painted to obtain the solid three-piece ball according to the present invention.

As described above, according to the present invention, it is possible to obtain a solid three-piece golf ball of the type (1) or (2) having excellent rebound characteristics and carry distance as well as a high spin performance by adjusting the size and specific gravity as well as the hardness of each of the two pieces forming the core assembly.

The solid three-piece golf ball of the type (1) or (2) according to the present invention provides an excellent carry distance and a better control of the ball compared with a ball having a long roll distance since the golf ball according to the present invention will be least influenced by the ground condition of the field. The golf ball according to the present invention also has an adequate spin performance.

Furthermore, it is possible to control the trajectory of the golf ball of type (1) or (2) using the different moment of inertia of each ball. Therefore, a golfer may select a suitable ball depending on his swing characteristics, such as, his club head speed, spinning ability and launching angle.

EXAMPLE 1

A starting mixture was prepared, which contained Cis-1, 4 polybutadiene rubber (base rubber), zinc diacrylate (co-cross linking agent), zinc oxide (filler), dicu-

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myl peroxide (initiator), 2,2'-methylene-bis (4-methyl-6-t-butyl phenol) (antioxidant) in the amounts as indicated in the Table 1.

The mixture was mixed and kneaded by using a two roll mill for 30 minutes and pressure-molded at 165° C for 10 minutes to prepare a solid inner core.

The inner core was covered by hemispherical pre-mold outer layers in a mold and the resultant product was cured by heating at 150° C. for 20 minutes to obtain a two-piece solid core assembly. This core assembly was then covered by ionomer resin with same dimple design by injection molding and then painted to provide a solid three-piece golf ball according to the present invention.

A solid two-piece golf ball was also prepared exactly in same way as the above.

24 of each type of golf ball were prepared which include the two types of solid three-piece golf ball (1, 2 in the Table 1) and the solid two-piece golf ball (3 in the Table 1). The golf balls were tested by a swing robot at a U.S. testing organization on the same day. The results of the tests are tabulated in the Table 1.

The test club used was 9.5° Driver Steel S. Shaft made by Taylor Made Golf Co. and the head speed was 108 miles/hour. The trajectory was measured through a wire screen within one inch square increments. The

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range was 0 to 10. The number was recorded at the point which the ball reached its apex. These numbers are for reference only to other balls in the test.

EXAMPLE 2

The starting mixture was prepared, which contained Cis-1, 4 polybutadiene rubber (rubber), zinc diacrylate (co-cross linking agent), zinc oxide (filler), dicumyl peroxide, N-butyl-4,4'-bis (t-butylperoxy) valerate (initiator), 2,2'-methylene-bis (4-methyl-6-t-butyl phenol) (antioxidant) in the amounts as indicated in the Table 2.

Solid three-piece balls were prepared with the process of the Example 1.

The solid three-piece balls (two types) according to the present invention were prepared and tested (1 and 2 in Table 2).

For comparison tests, three-piece solid golf balls commercially available (3 in Table 2) and thread wound balls (4 in Table 2) were also tested. 24 balls for each type of golf balls were used and tested under same method and conditions on the same day. The results of the tests are tabulated in Table 2.

From the Tables 1 and 2, it has been clearly proved that the solid three-piece golf ball according to the present invention has an excellent rebound characteristics, carry distance and an adequate spin performance.

TABLE 1

		Example		Comparative Example
		1	2	3
Starting mixture	Composition of inner core (parts by weight)			
	Cis-1,4 polybutadiene rubber	100	100	100
	zinc diacrylate	43	43	40
	zinc oxide	24.6	4.4	12.1
	dicumyl peroxide (40%)	3	3	3
	2,2'-methylene-bis(4-methyl-6-t-butyl phenol)	0.5	0.5	0.5
	Composition of out layer (parts by weight)			
	Cis-1,4 polybutadiene rubber	100	100	
	zinc diacrylate	35	35	
	zinc oxide	5.5	21.5	
	dicumyl peroxide (40%)	3	3	
	2,2'-methylene-bis(4-methyl-6-t-butyl phenol)	0.5	0.5	
	Composition of cover (parts by weight)			
	"Surly 8940" made by Du Pont	100	100	100
	Titanium dioxide	3.1	3.1	3.1
Physical Properties	Inner Core			
	Diameter (mm)	29.7	29.7	
	Weight (gr)	16.5	15	
	Specific gravity	1.20	1.09	
	Outer Core			
	Outer diameter (mm)	38.7	38.7	38.7
	Weight of core assembly (gr)	35.3	35.6	35.3
	Cover			
	Diameter of finished ball (mm)	42.7	42.7	42.7
	Weight of finished ball (gr)	45.3	45.5	45.3
	Distribution of hardness (Shore D)			
	Center	42	42	38
	Site 5 mm apart from center	53	50	47
	Site 10 mm apart from center	54	52	49
	Site 14 mm apart from center	61	58	49
	Site 15 mm apart from center	56	55	49
	Site 16 mm apart from center	55	54	55
	Site 18 mm apart from center	55	54	60
		126	122	122
Characteristics	Carry distance (yds)	242.80	243.23	239.19
	Total distance (yds)	271.61	269.38	267.47
	Velocity (ft/sec)	235.76	234.78	234.48
	Trajectory	5.54	5.52	5.29

	Example	Comparative Example

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TABLE 1-continued

		1	2	3	4
Starting mixture	Composition of inner core (parts by weight)				
	Cis-1,4 polybutadiene rubber	100	100		
	zinc diacrylate	38	40		
	zinc oxide	34.2	6		
	dicumyl peroxide (40%)	3	3		
	2,2'-methylene-bis(4-methyl-6-t-butyl phenol)	0.5	0.5		
	Composition of out layer (parts by weight)				
	Cis-1,4 polybutadiene rubber	100	100		
	zinc diacrylate	32	29		
	zinc oxide	3	24.4		
	N-butyl-4,4'-bis(t-butylperoxy)valerate(40%)	3.5	3.5		
	2,2'-methylene-bis(4-methyl-6-t-butyl phenol)	0.5	0.5		
	Composition of cover (parts by weight)				
	"Surly 8940" made by Du Pont	100	100		
	Titanium dioxide	3.1	3.1		
Physical Properties	Inner Core				
	Diameter (mm)	29.7	29.7		
	Weight (gr)	17.1	15.2		
	Specific gravity	1.25	1.11		
	Outer Core				
	Outer diameter (mm)	38.7	38.7	38.3	
	Weight of core assembly (gr)	35.3	35.4	34.7	
	Cover				
	Diameter of finished ball (mm)	42.7	42.7	42.8	42.7
	Weight of finished ball (gr)	45.3	45.3	45.0	45.5
	Distribution of hardness (Shore D)				
	Center	38	39		
	Site 5 mm apart from center	45	46		
	Site 10 mm apart from center	45	47		
	Site 14 mm apart from center	52	53		
	Site 15 mm apart from center	45	39		
	Site 16 mm apart from center	44	38		
	Site 18 mm apart from center	44	38		
		108	104	122	90
Characteristics	Carry distance (yds)	223.12	223.87	213.20	221.79
	Total distance (yds)	253.04	256.12	248.00	251.83
	Velocity (ft/sec)	235.67	235.46	233.41	231.23
	Trajectory	5.26	5.28	4.80	5.12

We claim:

1. A solid three-piece golf ball comprising a core assembly provided by an inner core 1 and an outer layer 2 and a cover 3 characterized by the following features:
a) the inner core 1 has a diameter in the range 23–35 mm and hardness (Shore D) in the range 30–62;
b) the outer layer 2 has a diameter in the range 36–41 mm and hardness (Shore D) in the range 30–56;
c) the golf ball has a maximum hardness (Shore D) in the range of 46–62 at the outer site of the inner core which is located at the interface between the inner core 1 and the outer layer 2 of the golf ball and the hardness then decreases both inwardly and outwardly.

2. A solid three-piece golf ball according to claim 1, in which the specific gravities of the inner core 1 and the outer layer 2 are in the ranges 1.15–1.50 and 1.00–1.20, respectively.

3. A solid three-piece golf ball according to claim 1, in which the specific gravities of the inner core 1 and the outer layer 2 are in the ranges 1.00–1.20 and 1.15–1.80, respectively.

4. A solid three-piece golf ball according to any one of claims 1–3, in which the site of maximum hardness is located 11.5–17.5 mm from the center of the ball.

5. A solid three-piece ball according to any one of claims 1–3 in which the minimum hardness (Shore D) difference between the said outer site in the inner core 1 and the site in the outer layer 2 of the ball is 3.

* * * * *

US005184828A

REEXAMINATION CERTIFICATE (2619th)

United States Patent [19]

Kim et al.

[11] **B1 5,184,828**

[45] Certificate Issued   Jul. 4, 1995

[54] **SOLID THREE-PIECE GOLF BALL**

[75] Inventors: **Moon K. Kim; In H. Hwang**, both of Seoul, Rep. of Korea

[73] Assignee: **Ilya Co., Ltd.**, Seoul, Rep. of Korea

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[51] Int. Cl.^{6} A63B 37/06
[52] U.S. Cl. 273/228; 273/230
[58] Field of Search 273/62, 218, 219, 220, 273/225, 228, 229, 230

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Primary Examiner—George J. Marlo

[57]   ABSTRACT

A non-wound three-piece golf ball which comprises an inner core, an outer layer and a cover, the inner core having a diameter of 23-35 mm and a hardness (Shore D) of 30-62, the outer layer having a diameter of 36-41 mm and a hardness (Shore D) of 30-56, the golf ball having a hardness (Shore D) 46-62 at the outer site in the inner core, which is 11.5-17.5 mm apart from the center of the ball. The golf ball has a maximum hardness (Shore D) in the range of 46-62 at the outer site of the inner core which is located at the interface between the inner core 1 and the outer layer 2 of the golf ball and the hardness then decreases both inwardly and outwardly.

FROM CENTER   SHORE D
11.5 - 17.5 $^m/_m$ apart   46-62

CENTER   A. SHORE D 30-48
5 $^m/_m$ apart   B. SHORE D 40-35
10 $^m/_m$ apart   C. SHORE D 43-58
14 $^m/_m$ apart   D. SHORE D 46-62
18 $^m/_m$ apart   E. SHORE D 30-56
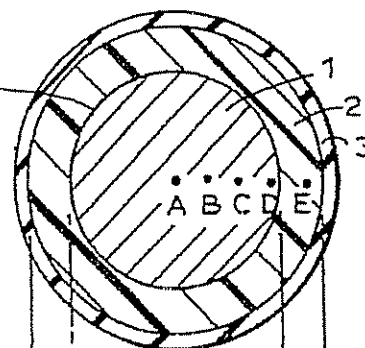
23-35mm
SHORE D
30-62

36-41mm
SHORE D
30-56

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REEXAMINATION CERTIFICATE
ISSUED UNDER 35 U.S.C. 307

NO AMENDMENTS HAVE BEEN MADE TO
THE PATENT

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AS A RESULT OF REEXAMINATION, IT HAS
BEEN DETERMINED THAT:

The patentability of claims 1–5 is confirmed.

* * * * *

EXHIBIT T

US005553852A

United States Patent [19]

Higuchi et al.

[11] Patent Number: 5,553,852

[45] Date of Patent: Sep. 10, 1996

[54] THREE-PIECE SOLID GOLF BALL

[75] Inventors: Hiroshi Higuchi; Hisashi Yamagishi, both of Yokohama; Yoshinori Egashira, Hidaka; Tadatoshi Yamada, Mitaka, all of Japan

[73] Assignee: Bridgestone Sports Co., Ltd., Tokyo, Japan

[21] Appl. No.: 271,953

[22] Filed: Jul. 8, 1994

[30]   Foreign Application Priority Data

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[51] Int. Cl.^{6} A63B 37/06
[52] U.S. Cl. 473/373; 473/378
[58] Field of Search 273/228, 230, 273/218, 220, 219, 225, 229, 214, 217

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Primary Examiner—George J. Marlo
Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak & Seas

[57]   ABSTRACT

A three-piece solid golf ball comprising a center core, an intermediate layer, and a cover. The center core (1) has a diameter of at least 29 mm, a hardness in the range of 45–80 JIS C and a specific gravity of less than 1.4. The intermediate layer (2) has a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale. The cover (3) has a thickness of 1–3 mm and a hardness of 50–85 JIS C. The ball has a good total balance of properties in that feeling and controllability are improved at no sacrifice of flying performance and durability.
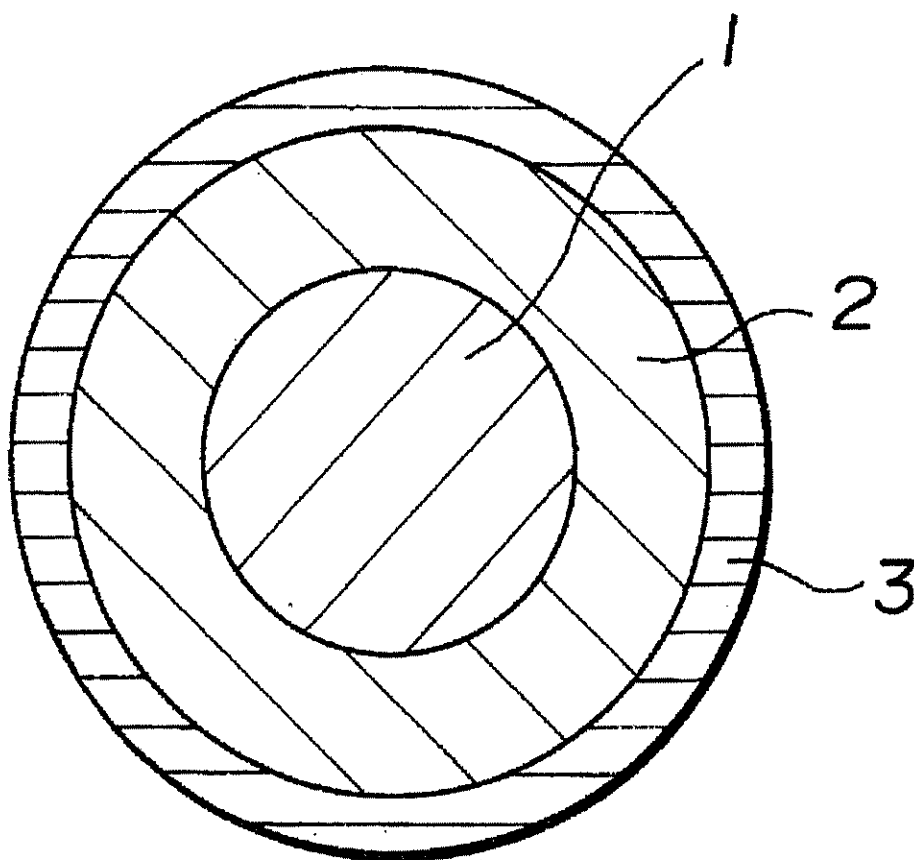
8 Claims, 1 Drawing Sheet
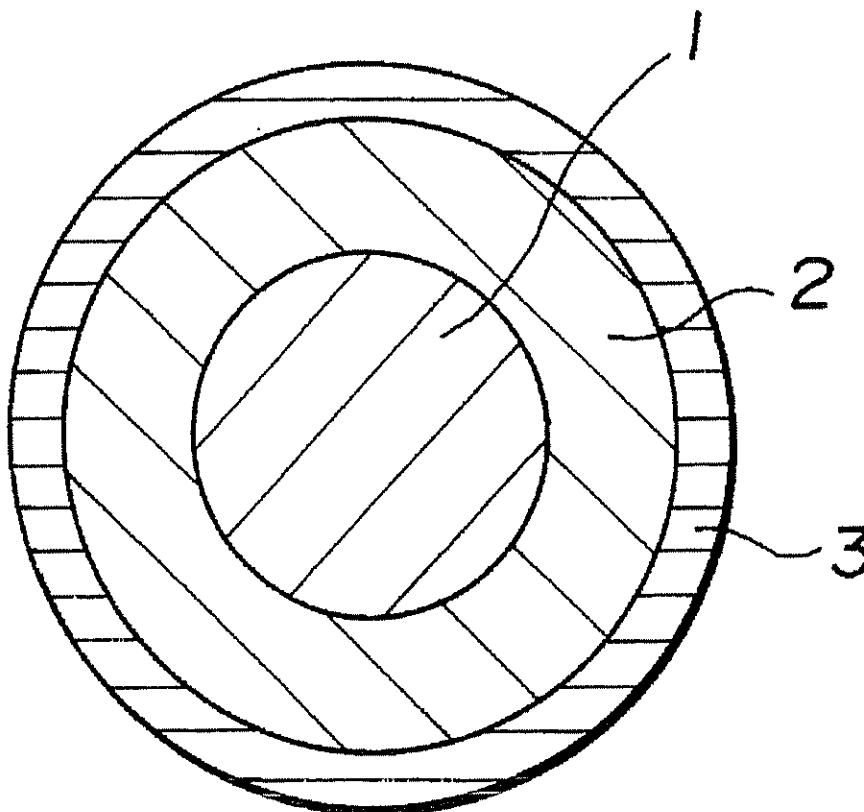
U.S. Patent   Sep. 10, 1996   5,553,852

FIG.1

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THREE-PIECE SOLID GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to three-piece solid golf balls comprising a center core, an intermediate layer, and a cover and more particularly, to three-piece solid golf balls which are improved in feeling on impact, controllability, and durability.

2. Prior Art

Among a variety of golf balls, thread-wound golf balls and solid golf balls are now popular. The solid golf balls are currently increasing to be a mainstream product. Among them, two-piece solid golf balls consisting of a core and a cover are most widespread.

Most amateur golfers are fond of two-piece solid golf balls which have excellent flying performance and durability although these balls have the disadvantages of a very hard feel on hitting and low control due to rapid ball separation on hitting. For this reason, many of professional golfers and skilled amateur golfers who impose weight on feeling and control prefer wound golf balls, especially wound golf balls using a soft balata cover, to two-piece solid golf balls. The wound golf balls are superior in feeling and control, but inferior in flying distance and durability to the two-piece solid golf balls.

Under the present situation that two-piece solid golf balls and wound golf balls have contradictory characteristics as mentioned above, players make a choice of golf balls depending on their own skill and taste.

In order to develop solid golf balls having a hitting feel approximate to the wound golf balls, two-piece solid golf balls of the soft type have been considered. For such two-piece solid golf balls of the soft type, soft cores must be used. If the cores are soft, however, repulsion becomes low with a concomitant loss of flying performance and durability is considerably deteriorated. That is, the superior flying performance and durability which are a characteristic of two-piece solid golf balls are lost, and in an extreme case, the balls become unacceptable for practical use.

Controllability, which is required even on full shots with drivers, is most important on control shots like approach shots. In an exemplary situation that the next shot should fly beyond the bunker and a short distance from the green edge to the cup, the player who is either professional or amateur will naturally wish to hit a ball with a minimal run. Such controllability of a golf ball largely depends on spin properties.

On a full shot with a club having a relatively large loft, the club loft is dominant to that the ball itself so that almost all balls are given an appropriate amount of spin and few balls overrun. However, on an approach shot over a short distance of 30 or 50 yards, balls will significantly vary in run or controllability. The major factor causing such a difference is not a basic structure, but the identity of cover material. In two-piece solid golf balls, however, covers made of soft material are effective for improving controllability, but detrimental for gaining flying distance.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a solid golf ball which is improved in feeling and controllability while maintaining the superior flying performance

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and durability which are characteristic of solid golf balls, that is, improved in total balance.

In connection with a solid golf ball having a core forming the center and a cover forming the outermost layer, the inventors have found that by providing a relatively hard intermediate layer between the center core and the cover, and controlling the size and specific gravity of the core, intermediate layer and cover, the center core and core can be made relatively soft to improve feeling and controllability without deteriorating flying performance and durability. The feeling and controllability can be improved in a favorable way.

Briefly stated, an intermediate layer having a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale is formed around a center core having a diameter of at least 29 mm and a specific gravity of less than 1.4 and greater than the intermediate layer specific gravity. A cover having a thickness of 1 to 3 mm is formed on the outer surface of the intermediate layer to complete a solid golf ball. Then even when the center core is softened to a JIS C scale hardness of 45 to 80 and the cover softened to a JIS C scale hardness of 50 to 85, the feeling and controllability can be improved at no sacrifice of flying distance and durability. Further when the intermediate layer is formed of a resin composition based on a high repulsion ionomer resin, the hitting feel and controllability can be further improved with no sacrifice of flying distance and durability.

The present invention provides a three-piece solid golf ball comprising a center core, an intermediate layer, and a cover wherein the center core has a diameter of at least 29 mm and a specific gravity of less than 1.4, the intermediate layer has a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale. The cover has a thickness of 1 to 3 mm. The specific gravity of the intermediate layer is lower than the specific gravity of the center core. In one preferred embodiment, the intermediate layer is formed of a composition based on a high repulsion ionomer resin.

BRIEF DESCRIPTION OF THE DRAWING

The sole figure, FIG. 1 is a schematic cross section of a three-piece solid golf ball according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, there is schematically illustrated a typical three-piece solid golf ball according to the invention. The ball includes a spherical center core 1 forming the center of the ball and a cover 3 forming the outermost layer of the ball. A relatively hard intermediate layer 2 is disposed between the core 1 and the cover 3. The size and specific gravity of the core 1, intermediate layer 2, and cover 3 are set in specific ranges.

The center core has a diameter of at least 29 mm, preferably 29 to 37 mm and a specific gravity of less than 1.4, preferably 1.05 to 1.38. With a diameter of less than 29 mm, the intermediate layer must be relatively thick with losses of repulsion and feeling. With a specific gravity of 1.4 or more, the ball has a heavier weight which exceeds the weight requirement of golf balls.

On an impact entailing substantial deformation as found on driver shots, the player gets a feeling which largely depend on the hardness of the center core 1 and varies with the club head speed given by the player. Therefore, the

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hardness of the center core 1 should be set in accordance with the head speed of the target players. In this sense, the center core hardness is not particularly limited although it preferably ranges from 45 to 80, more preferably from 60 to 80 on JIS C scale (at the center core surface).

The center core 1 is generally formed from a well-known rubber composition comprising a base rubber, co-crosslinking agent and peroxide through heating, pressing and molding steps. The base rubber may be one conventionally used in solid golf balls and preferably be selected from polybutadiene rubber and mixtures of polybutadiene rubber and polyisoprene rubber. Use of 1,4-polybutadiene rubber containing more than 90% of cis structure is preferred for high repulsion. The co-crosslinking agents used in conventional solid golf balls include zinc and magnesium salts of unsaturated fatty acids such as methacrylic acid and acrylic acid and esters of unsaturated fatty acids such as trimethylpropane trimethacrylate and they may be used in the present invention. Zinc acrylate is preferred for high repulsion. The co-crosslinking agent is blended in amounts of about 15 to 30 parts by weight per 100 parts by weight of the base rubber. The peroxide may be selected from a variety of peroxides, preferably dicumyl peroxide and mixtures of dicumyl peroxide and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane. The peroxide is blended in amounts of about 0.5 to 1 part by weight per 100 parts by weight of the base rubber. If desired, zinc oxide and barium sulfate may be blended in the rubber composition for specific gravity adjustment while antioxidants may also be blended.

The intermediate layer 2 has a radial thickness of at least 1 mm, preferably 1.5 to 3.5 mm, a specific gravity of less than 1.2, preferably 0.9 to 1 and lower than the center core specific gravity, and a hardness of at least 85, preferably 85 to 100 on JIS C scale. With a thickness of less than 1 mm, repulsion is lowered to reduce flying distance. With a specific gravity of 1.2 or more, the center core must have a relatively low specific gravity so that the golf ball may be increased in inertia moment and reduced in spin property and thus lose some controllability. A similar detrimental effect is observed when the intermediate layer specific gravity is greater than the center core specific gravity. A layer with a JIS C scale hardness of less than 85 detracts from flying performance. The intermediate layer preferably has an outer diameter of 38 to 41 mm though not limited thereto. Also preferably the difference in specific gravity between the center core and the intermediate layer is 0.1 or more, especially 0.1 to 0.5 though not limited thereto.

The intermediate layer 2 is effective in compensating for lowering repulsion of the center core 1 which is made soft. It is then formed of a relatively hard (JIS C scale hardness≧85), repulsive material. Although the material is not critical, preferred materials are ionomer resins, for example, Himilan 1706 and 1605 commercially available from Mitsui-dupont Polychemical K.K. and Surlyn commercially available from E.I. dupont. A 1:1 blend of Himilan 1706 and Himilan 1605 is most preferred. In addition to the ionomer resin, the composition of which the intermediate layer is formed may further contain weight control agents, for example, inorganic fillers such as zinc oxide and barium sulfate, coloring agents such as titanium dioxide, and other additives.

The cover 3 has a radial thickness of 1 to 3 mm, preferably 1.5 to 2.5 mm. A cover more than 3 mm thick is low in repulsion whereas a cover less than 1 mm thick is low in durability such as cut resistance. Although the hardness of the cover 3 is not particularly limited, it is preferably set in a relatively soft range of 50 to 85, more preferably 60 to 85 on JIS C scale because in this range, improvements in all of repulsion (flying performance), durability and controllability are expected.

The cover 3 is generally formed of resinous materials which are conventionally used as the cover of solid golf balls, preferably those materials which are relatively soft (JIS C scale hardness 50 to 85) and highly repulsive. Examples include ionomer resins such as Himilan 1650 commercially available from Mitsui-dupont Polychemical K.K., Surlyn 8120 commercially available from E.I. dupont, and mixtures thereof, thermoplastic polyester elastomers such as Hytrel 4047 commercially available from Toray-dupont K.K., and balata resins. If necessary, inorganic fillers may be blended in these resins for coloring purposes.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

Examples and Comparative Examples

Using a center core, intermediate layer, and cover having the composition shown in Table 1, three-piece solid golf balls (Examples 1–6, Comparative Examples 1–3) were prepared. The center core was prepared by kneading the respective components in a roll mill and pressure molding at 155° C. for 15 minutes. The intermediate layer was formed by injection molding so as to enclose the outer surface of the center core. The cover was formed around the intermediate layer by injection molding. The three-piece solid golf balls were completed in this way. The parameters associated with the core, intermediate layer and cover are shown in Table 2.

The golf balls were evaluated for spin characteristic, flying performance, feeling, and durability by the following tests. The results are shown in Table 2.

Spin Characteristic

Using a swing robot manufactured by True Temper Co., the ball was hit by the driver at a head speed of 45 m/s (abbreviated as W1 HS45 in Table 2) and by the sand wedge at a head speed of 17.6 m/s (abbreviated as SW HS17.6 in Table 2). The ball spin (rpm) was observed using a science eye (manufactured by Bridgestone Corporation).

Feeling

Professional golfers evaluated a feeling on impact according to the following criterion.

O: good
Δ: average
×: poor

Flying Performance

In the spin and feeling tests, the flying distance the ball traveled was also measured. Total evaluation was made according to the following criterion.

O: good
Δ: average
×: poor

Durability

Using a flywheel hitting machine, the ball was repeatedly hit at a head speed of 38 m/s until the ball was broken. With the number of hits counted, the ball was rated according to the following criterion.

O: good
Δ: average
×: poor

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TABLE 1

	Example						Comparative Example		
	1	2	3	4	5	6	1	2	3
Center core									
Cis-1,4-polybutadiene	100	100	100	100	100	100	100	100	100
Zinc acrylate	20	20	20	30	20	20	20	25	20
Zinc oxide	56	36	36	20	23	10	90	25	55
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Dicumyl peroxide	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Intermediate layer									
Himilan 1706	50	50	50	50	50	50	50	50	50
Himilan 1605	50	50	50	50	50	50	50	50	50
Cover									
Himilan 1650	50	50	50			50	50		50
Surlyn 8120	50	50	50			50	50		50
Hytrel 4047				100				100	
Trans-isoprene rubber					90				
Natural rubber					10				

Note:
The amounts of components blended are parts by weight and their proportion is independent among the center core, intermediate layer, and cover.

TABLE 2

	Example						Comparative Example		
	1	2	3	4	5	6	1	2	3
Center core									
Outer diameter, mm	31.52	35.28	35.28	35.28	35.29	36.40	27.68	35.24	31.52
Hardness, JIS C	66	66	66	79	66	66	66	73	66
Specific gravity	1.36	1.24	1.24	1.19	1.16	1.07	1.56	1.19	1.35
Intermediate layer									
Thickness, mm	3.4	1.7	2.2	2.2	1.7	2.0	5.7	1.8	1.6
Hardness, JIS C	91	91	91	91	91	91	91	82	91
Specific gravity	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.97	0.95
Outer diameter, mm	38.35	38.73	39.65	39.66	38.73	40.40	39.00	38.91	34.56
Cover									
Thickness, mm	2.2	2.0	1.5	1.5	2.0	1.8	1.8	1.9	4.0
Specific gravity	0.97	0.97	0.97	1.10	1.13	0.97	0.97	1.10	0.97
Hardness, JIS C	82	82	82	61	78	82	82	61	82
Ball									
Outer diameter, mm	42.68	42.67	42.67	42.70	42.70	44.00	42.65	42.63	42.65
Weight, g	45.50	45.45	45.50	45.55	45.53	45.60	45.50	45.55	45.50
Performance									
Spin (rpm) W1 HS45	3300	3020	3030	3920	3600	3030	35	3600	3250
SW HS17.6	3900	4000	4300	6390	5800	4100	4100	4050	3500
Feeling	Δ	O	O	Δ	O	O	X	O	O
Flying performance	O	O	O	O	Δ	O	X	X	X
Durability	O	O	O	O	O	O	O	O	O

As is evident from Table 2, the three-piece solid golf balls of the present invention have a good balance of properties in that the center core and cover can be made soft to ensure a pleasant feeling and controllability (spin) without deteriorating flying performance and durability.

There has been described a three-piece solid golf ball which includes a core, intermediate layer and cover having controlled size, hardness and specific gravity so that the ball has a good total balance of properties in that a relatively soft center core and cover are used to ensure a pleasant feeling and controllability at no sacrifice of flying performance and durability.

Japanese Patent Application No. 5-193065 is incorporated herein by reference.

Although one preferred embodiment have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A three-piece solid golf ball comprising;

a center core, an intermediate layer, and a cover enclosing the core through the intermediate layer,

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said center core having a diameter of at least 29 mm and a specific gravity of less than 1.4,

said intermediate layer having a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale, the specific gravity of said intermediate layer being lower than the specific gravity of said center core, and

said cover having a thickness of 1 to 3 mm and being softer than said intermediate layer.

2. The golf ball of claim 1 wherein said intermediate layer is formed of a high repulsion ionomer resin base composition.

3. The golf ball of claim 1 wherein said center core has a hardness of 45 to 80 on JIS C scale and said cover has a hardness of 50 to 85 on JIS C scale.

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4. The golf ball of claim 1 wherein said center core is comprised of a polybutadiene base rubber composition.

5. The golf ball of claim 1 wherein the diameter of said center core is in the range of 29–37 mm.

6. The golf ball of claim 1 wherein a difference in the specific gravity between the center core and the intermediate layer is in the range of 0.1 to 0.5.

7. The golf ball of claim 1 wherein the specific gravity of said intermediate layer is in the range of 0.9 to 1.0.

8. The golf ball of claim 1 wherein the hardness of said intermediate layer is in the range of 85–100 on JIS C.

*   *   *   *   *

EXHIBIT U

IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

BRIDGESTONE SPORTS CO., LTD.,
and BRIDGESTONE GOLF, INC.,

        Plaintiffs,

    v.

ACUSHNET COMPANY,

        Defendant.

C.A. No. 05-132 (JJF)

PLAINTIFFS' SUPPLEMENTAL RESPONSES TO DEFENDANT'S FIRST SET OF REQUESTS FOR ADMISSION (NOS. 21-22)

Pursuant to Rules 26 and 36 of the Federal Rules at Civil Procedure, Plaintiffs Bridgestone Sports Co., Ltd. and Bridgestone Golf, Inc. (individually or collectively "Bridgestone") hereby supplement their prior response to Defendant's First Set of Requests for Admission dated December 13, 2005.

GENERAL OBJECTIONS

The General and Specific Objections set forth in Plaintiffs' Responses to Defendant's First Set of Requests for Admission (Nos. 1-22) served on January 17, 2006 are incorporated herein by reference. Subject to and without waiving any of the General and Specific Objections, Bridgestone hereby supplements its responses to Request for Admission Nos. 21 and 22.

REQUEST FOR ADMISSION NO. 21

Admit that you have tested the outer cover thickness of the Titleist™ Pro V1 golf ball to be less than 1 mm.

RESPONSE TO REQUEST FOR ADMISSION NO. 21:

In addition to the General objections, Bridgestone specifically objects to the Request as being vague and ambiguous because it is unclear whether "1 mm" is intended to be a claim

limitation, and as being premature because to the extent "1 mm" refers to the claim limitations of

the '852 patent the Court has not yet construed this phrase. Bridgestone further objects to the

phrase "tested the outer cover thickness of the Titleist™ Pro V1" and as being vague and

ambiguous. Bridgestone further objects to the Request as seeking privileged information,

information covered by the attorney work product doctrine, and/or information for settlement

purposes under FRE 408.

Subject to and without waiving the general and specific objections, Bridgestone admits

that it has measured the outer cover thickness of a Titleist™ Prov V1 golf ball to be within the

scope of the claim 1 of the '852 patent

SUPPLEMENTAL RESPONSE TO REQUEST FOR ADMISSION NO. 21:

Subject to and without waiving the general and specific objections, Bridgestone admits

that a member of its staff measured the outer cover thickness of the Titleist™ Pro V1 to be less

than 1 mm.

REQUEST FOR ADMISSION NO. 22:

Admit that you have tested the outer cover thickness of the Titleist™ Pro V1x golf ball to

be less than 1 mm.

RESPONSE TO REQUEST FOR ADMISSION NO. 22:

In addition to the General objections, Bridgestone specifically objects to the Request as

being vague because it is unclear whether "1 mm" is intended to be a claim limitation, and as

being premature because to the extent "1 mm" refers to the claim limitations of the '852 patent

the Court has not yet construed this phrase. Bridgestone further objects to the phrase "tested the

outer cover thickness of the Titleist™ Pro V1x" as being vague and ambiguous. Bridgestone

further objects to the Request as seeking privileged information and information covered by the

attorney work product doctrine, and/or seeking information for settlement purposes under FRE

408.

Subject to and without waiving the general and specific objections, Bridgestone admits

that it has measured the outer cover thickness of a Titleist™ Prov V1x golf ball to be within the

scope of the claim 1 of the '852 patent.

SUPPLEMENTAL RESPONSE TO REQUEST FOR ADMISSION NO. 22:

Subject to and without waiving the general and specific objections, Bridgestone admits

that a member of its staff measured the outer cover thickness of the Titleist™ Pro V1x to be less

than 1 mm.

MORRIS, NICHOLS, ARSHT & TUNNELL LLP

Jack B. Blumenfeld (#1014)
Maryellen Noreika (#3208)
Leslie A. Polizoti (#4299)
1201 N. Market Street
P.O. Box 1347
Wilmington, DE 19801
(302) 658-9200
Attorneys for Plaintiffs

OF COUNSEL:

Robert M. Masters
PAUL, HASTINGS,
  JANOFSKY & WALKER LLP
825 15th Street, N.W.
Washington, DC 20005
(202) 551-1700

March 27, 2006

CERTIFICATE OF SERVICE
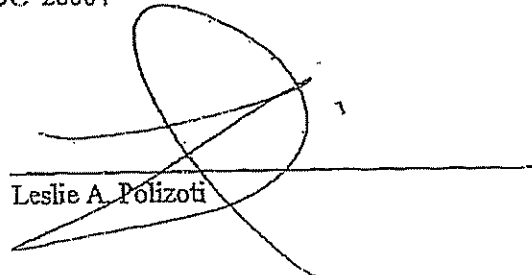
I certify that copies of the foregoing were caused to be served this 27th day of

March, 2006 upon the following in the manner indicated:

BY HAND

David E. Moore
Potter Anderson & Corroon LLP
1313 N. Market Street
Wilmington, DE 19801

BY FACSIMILE

Alan M. Grimaldi
Howrey LLP
1299 Pennsylvania Avenue, NW
Washington, DC 20004

Leslie A. Polizoti

IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

BRIDGESTONE SPORTS CO., LTD.,   )
and BRIDGESTONE GOLF, INC.,   )
)
            Plaintiffs,   )   C.A. No. 05-132 (JJF)
)
    v.   )
)
ACUSHNET COMPANY,   )
)
            Defendant.   )

NOTICE OF SERVICE

I certify that copies of Plaintiffs' Supplemental Responses to Defendant's First

Set of Requests for Admission (Nos. 21-22) were caused to be served on March 27, 2006 upon

the following in the manner indicated:

BY HAND

David E. Moore
Potter Anderson & Corroon LLP
1313 N. Market Street
Wilmington, DE 19801

BY FACSIMILE

Alan M. Grimaldi
Howrey LLP
1299 Pennsylvania Avenue, N.W.
Washington, DC 20004

MORRIS, NICHOLS, ARSHT & TUNNELL LLP

/s/ Leslie A. Polizoti
Jack B. Blumenfeld (#1014)
Maryellen Noreika (#3208)
Leslie A. Polizoti (#4299)
1201 N. Market Street
P.O. Box 1347
Wilmington, DE 19801
(302) 658-9200
  Attorneys for Bridgestone Sports Co., Ltd.
  and Bridgestone Golf, Inc.

OF COUNSEL:

Robert M. Masters
Paul, Hastings, Janofsky & Walker LLP
825 15th Street, N.W.
Washington, DC 20005
(202) 551-1700

March 27, 2006

2

CERTIFICATE OF SERVICE

I certify that on March 27, 2006, I electronically filed the foregoing Notice of

Service with the Clerk of the Court using CM/ECF, which will send notification of such filing(s)

to David E. Moore.

I further certify on March 27, 2006, copies of the foregoing document were

served upon counsel of record in the manner indicated:

BY HAND

David E. Moore, Esquire
Potter Anderson & Corroon LLP
1313 N. Market Street
Wilmington, DE 19801

BY FACSIMILE

Alan M. Grimaldi, Esquire
Howrey LLP
1299 Pennsylvania Avenue, NW
Washington, DC 20004

/s/ Leslie A. Polizoti
Leslie A. Polizoti (#4299)
1201 N. Market Street
P.O. Box 1347
Wilmington, DE 19899
(302) 658-9200
lpolizoti@mnat.com

EXHIBIT V

US006818705B2

(12) **United States Patent**
Wu et al.

(10) Patent No.: **US 6,818,705 B2**
(45) Date of Patent: **Nov. 16, 2004**

(54) **THIN-LAYER-COVERED GOLF BALL WITH IMPROVED VELOCITY**

(75) Inventors: **Shenshen Wu**, North Dartmouth, MA (US); **Edmund A. Hebert**, Fairhaven, MA (US); **Laurent Bissonnette**, Portsmouth, RI (US); **David A. Bulpett**, Boston, MA (US); **Murali Rajagopalan**, South Dartmouth, MA (US); **Peter Voorheis**, Fall River, MA (US); **Mark N. Wrigley**, New Bedford, MA (US)

(73) Assignee: **Acushnet Company**, Fairhaven, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 90 days.

(21) Appl. No.: 10/256,011

(22) Filed: **Sep. 27, 2002**

(65) **Prior Publication Data**

US 2003/0096915 A1 May 22, 2003

Related U.S. Application Data

(63) Continuation of application No. 09/721,740, filed on Nov. 27, 2000, now Pat. No. 6,486,261, which is a continuation-in-part of application No. 09/461,736, filed on Dec. 16, 1999, now Pat. No. 6,465,578, and a continuation-in-part of application No. 09/311,591, filed on May 14, 1999, now Pat. No. 6,210,294, and a continuation-in-part of application No. 09/274,015, filed on Mar. 22, 1999.

(60) Provisional application No. 60/113,949, filed on Dec. 24, 1998.

(51) Int. Cl.[7] A63B 37/12; A63B 37/06

(52) U.S. Cl. 525/261; 525/274; 473/373; 473/374; 473/377

(58) Field of Search 525/261, 274; 473/373, 374, 377

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Primary Examiner—David J. Buttner
(74) *Attorney, Agent, or Firm*—Swidler Berlin Shereff Friedman, LLP

(57) **ABSTRACT**

A golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 200,000 and a resilience index of at least about 40; and a cover layer comprising a polyurethane composition formed from a pre-polymer having no greater than 7.5 percent by weight unreacted isocyanate groups.

22 Claims, 1 Drawing Sheet

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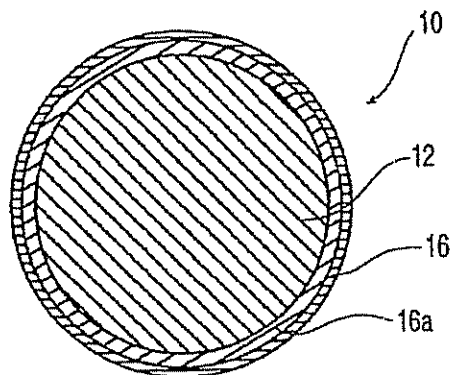
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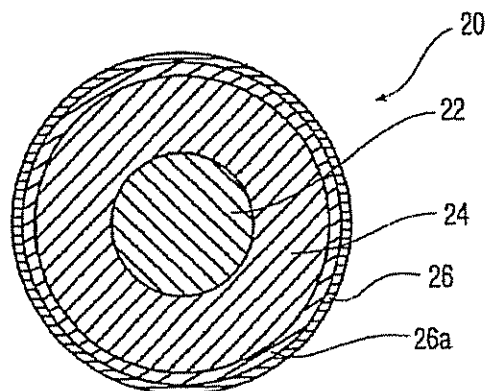
Fig. 2
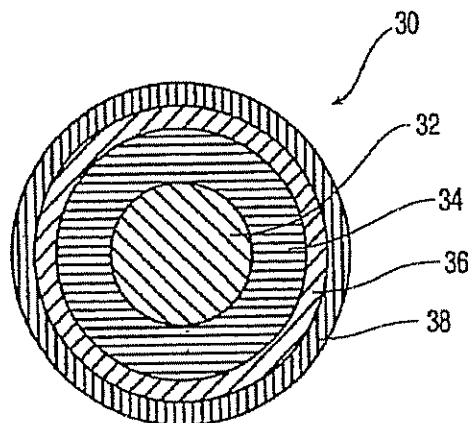
Fig. 3

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THIN-LAYER-COVERED GOLF BALL WITH IMPROVED VELOCITY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 09/721,740, filed Nov. 27, 2000, now U.S. Pat No. 6,486,261, which is a continuation-in-part of U.S. patent application Ser. No. 09/461,736, filed Dec. 16, 1999, now U.S. Pat. No. 6,465,578, which claims the benefit of U.S. Patent Provisional Application No. 60/113,949, filed Dec 24, 1998, and is a continuation-in-part of U.S. patent application Ser. No. 09/311,591, filed May 14, 1999, now U.S. Pat. No. 6,210,294, and also a continuation-in-part of U.S patent application Ser. No. 09/274,015, filed Mar. 22, 1999

FIELD OF THE INVENTION

The invention relates generally to golf balls and, more specifically, to golf balls with covers formed of a polymer blend comprising a polyurethane composition and cores formed of a polybutadiene composition. The polyurethane composition comprises a prepolymer of a polyisocyanate and a polyol, and a diamine curing agent. The polybutadiene composition comprises a butadiene polymer with a resilience index greater than about 40 and a molecular greater than about 200,000 The golf balls of the present invention have been found to provide improved velocity

BACKGROUND OF THE INVENTION

Conventional golf balls can be divided into several general classes: (a) solid golf balls having one or more layers, and (b) wound golf balls. Solid golf balls include one-piece balls, which are easy to construct and relatively inexpensive, but have poor playing characteristics and are thus generally limited for use as range balls. Two-piece balls are constructed with a generally solid core and a cover and are generally the most popular with recreational golfers because they are very durable and provide maximum distance. Balls having a two-piece construction are commonly formed of a polymeric core encased by a cover. Typically, the core is formed from polybutadiene that is chemically crosslinked with zinc diacrylate and/or other similar crosslinking agents. These balls are generally easy to manufacture, but are regarded as having limited playing characteristics. Solid golf balls also include multi-layer golf balls that are comprised of a solid core of one or more layers and/or a cover of one or more layers. These balls are regarded as having an extended range of playing characteristics.

Wound golf balls are generally preferred by many players due to their high spin and soft "feel" characteristics. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material and a cover. Wound balls generally are more difficult and expensive to manufacture than solid two-piece balls

A variety of golf balls have been designed by manufacturers to provide a wide range of playing characteristics. such as compression, velocity, "feel," and spin. These characteristics can be optimized for various playing abilities. One of the most common components that manufacturers have addresses for optimizing and/or altering the playing characteristics of golf balls, is the polymer components present in modern golf ball construction, in particular, golf ball centers and/or core. In addition to ionomers, one of the most common polymers employed is polybutadiene and, more specifically, polybutadiene having a high cis-isomer concentration.

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The use of a polybutadiene having a high cis-concentration results in a very resilient and rigid golf ball, especially when coupled with a hard cover material. These highly resilient golf balls have a relatively hard "feel" when struck by a club. Soft "feel" golf balls constructed with a high cis-polybutadiene have low resilience. In an effort to provide improved golf balls, various other polybutadiene formulations have been prepared, as discussed below.

U.S. Pat No. 3,239,228 discloses a solid golf ball having a core molded of polybutadiene rubber with a high sulfur content, and a cover. The polybutadiene content of the core is stereo-controlled to the configuration 25–100 percent cis- and 0–65 percent trans-1,4-polybutadiene, with any remainder having a vinyl configuration of polybutadiene. A preferred embodiment of the polybutadiene golf ball core contains 35 percent cis-, 52 percent trans-, and 13 percent vinyl-polybutadiene The level of trans- and vinyl-content are disclosed to be unimportant to the overall playing characteristics of the polymer blend

British Patent No. 1,168,609 discloses a molding composition from which improved golf ball cores can be molded and which contains cis-polybutadiene as a basic polymer component The core polymer component typically includes at least 60 percent cis-polybutadiene, with the remainder being either the trans- or vinyl-forms of polybutadiene. In a preferred embodiment, the core polybutadiene component contains 90 percent cis-configuration, with the remaining 10 percent being either the trans- or vinyl-configurations of 1,4-polybutadiene

U.S. Pat. Nos. 3,572,721 and 3,572,722 disclose a solid, one- or two-piece golf ball, with the two-piece ball having a core and a cover. The cover material can include any one of a number of materials, or blends thereof, known to those of ordinary skill in the art, including trans-polybutadiene which may be present in an amount from at least 90 percent, with the remainder being the cis- and/or vinyl configuration.

British Patent No. 1,209,032 discloses a two- or three-piece golf ball having a core and a cover The core or cover material can be any material capable of being crosslinked In particular, the material can be a polymer or a copolymer of butadiene or isoprene. Preferably, the polymer component is polybutadiene having a cis content of greater than 50 percent by weight.

U.S. Pat. No. 3,992,014 discloses a one-piece, solid golf ball. The golf ball material is typically polybutadiene, with a stereo-configuration selected to be at least 60 percent cis-polybutadiene, with the remaining 40 percent being the trans-polybutadiene and/or 1,2-polybutadiene (vinyl) isomers.

U.S. Pat. No. 4,692,497 discloses a golf ball and material thereof formed by curing a diene polymer including polybutadiene and a metal salt of an alpha, beta ethylenically unsaturated acid using at least two free radical initiators.

U.S. Pat. No. 4,931,376 discloses a process for producing butadiene polymers for use in various applications, including golf ball cover materials. One embodiment of the invention employs a blended polymeric resin material, including at least 30 percent by weight of a trans-polybutadiene polymer as a golf ball cover on a two-piece ball. In a preferred embodiment, the golf ball cover material contains a blend including 30 to 90 percent by weight of a trans-polybutadiene polymer.

U.S. Pat. No. 4,971,329 discloses a solid golf ball made from a polybutadiene admixture of cis-1,4 polybutadiene and 1,2 polybutadiene, a metal salt of an unsaturated carboxylic acid, an inorganic filler, and a free radical initiator

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The admixture has about 99.5 percent to about 95 percent by weight of cis-1,4 polybutadiene and about 0.5 percent to about 5 percent by weight of 1,2 polybutadiene.

U.S. Pat. No. 5,252,652 discloses a one-piece or multi-layered golf ball core with improved flying performance from a rubber composition comprising a base rubber, preferably 1,4-polybutadiene with a cis-content of at least 40 mole percent, an unsaturated carboxylic acid metal salt, an organic peroxide, and an organic sulfur compound and/or a metal salt thereof. The organic sulfur compound and/or a metal salt is typically present in an amount from about 0.05 to 2 parts per hundred by weight and the organic peroxide is typically present in an amount from about 0.5 to 3 parts per hundred by weight of the total polymer component.

European Patent No. 0 577 058 discloses a golf ball containing a core and a cover that is formed as two separate layers. The inner layer of the cover is molded over the core and is formed from ionomer resin. The outer layer of the cover is molded over the inner layer and is formed from a blend of natural or synthetic balata and a crosslinkable elastomer, such as polybutadiene. In one embodiment of the outer layer of the cover, the elastomer is 1,4-polybutadiene having a cis-structure of at least 40 percent, with the remaining 60 percent being the trans-isomer. A preferred embodiment contains a cis-structure of at least 90 percent and more preferably, a cis-structure of at least 95 percent.

U.S. Pat. No. 5,421,580 discloses a wound golf ball having a liquid center contained in a center bag, a rubber thread layer formed on the liquid center, and a cover over the wound layer and liquid center. The cover material can include any one of a number of materials, or blends thereof, known to those of ordinary skill in the art, including trans-polybutadiene and/or 1,2-polybutadiene (vinyl), such that the cover has a JIS-C hardness of 70–85; preferred trans-percentages are not disclosed.

U.S. Pat. No. 5,697,856 discloses a solid golf ball having a core and a cover wherein the core is produced by vulcanizing a base rubber composition containing a butadiene rubber having a cis-polybutadiene structure content of not less than 90 percent before vulcanization. The amount of trans-polybutadiene structure present after vulcanization is 10 to 30 percent, as amounts over 30 percent are alleged to detrimentally result in cores that are too soft with deteriorated resilience performance, and to cause a decrease in golf ball performance. The core includes a vulcanizing agent, a filler, an organic peroxide, and an organosulfur compound.

British Patent No. 2,321,021 discloses a solid golf ball having a core and a cover formed on the core and having a two-layered cover construction having an inner cover layer and an outer cover layer. The outer cover layer is comprised of a rubber composite that contains 0.05 to 5 parts by weight of an organic sulfide compound. The core rubber composition comprises a base rubber, preferably 1,4-polybutadiene having a cis-content of at least 40 percent by weight, a crosslinking agent, a co-crosslinking agent, an organic sulfide, and a filler. The crosslinking agent is typically an organic peroxide present in an amount from 0.3 to 5.0 parts by weight and the co-crosslinking agent is typically a metal salt of an unsaturated fatty acid present in an amount from 10 to 40 parts by weight. The organic sulfide compound is typically present from 0.05 to 5 parts by weight.

U.S. Pat. No. 5,816,944 discloses a solid golf ball having a core and a cover wherein the core has a JIS-C hardness of 50 to 80 and the cover has a Shore-D hardness of 50 to 60. The core material includes vulcanized rubber, such as cis-polybutadiene, with a crosslinker, an organic peroxide, an

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organosulfur compound and/or a metal-containing organo-sulfur compound, and a filler.

Additionally, conventional polymers that have a high percentage of the trans-polybutadiene conformation, such as DIENE 35NF, from Firestone Corp., that has 40 percent cis-isomer and 50 percent trans-polybutadiene isomer, and mixtures of high-cis- and high-trans-polybutadiene isomers, such as CARIFLEX BR1220, from Shell Corporation, and FUREN 88, from Asahi Chemical Co., respectively, typically do not yield high resilience values and therefore are not desirable.

In addition to changing center or core ingredients to affect golf ball performance characteristics, a number of patents have issued that are directed towards modifying the properties of layers and covers used in forming a variety of golf balls, such as wound balls, conventional solid balls, multi-layer balls having dual cover layers, dual core layers, and/or balls having a mantle layer disposed between the cover and the core. The most common polymers used by manufacturers in golf ball layers and covers have been ionomers, such as SURLYN, commercially available from E. I. DuPont de Nemours and Co., of Wilmington, Del. Recently, however, manufacturers have investigated the used of alternative polymers, such as polyurethane. For example, U.S. Pat. No. 3,147,324 is directed to a method of making a golf ball having a polyurethane cover.

Polyurethanes have been recognized as useful materials for golf ball covers since about 1960. Polyurethane is the product of a reaction between a polyurethane prepolymer and a curing agent. The polyurethane prepolymer is a product formed by a reaction between a polyol and a diisocyanate. The curing agents used previously are typically diamines or glycols. A catalyst is often employed to promote the reaction between the curing agent and the polyurethane prepolymer.

Since 1960, various companies have investigated the usefulness of polyurethane as a golf ball cover material. U.S. Pat. No. 4,123,061 teaches a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a diamine. U.S. Pat. No. 5,334,673 discloses the use of two categories of polyurethane available on the market, i.e., thermoset and thermoplastic polyurethanes, for forming golf ball covers and, in particular, thermoset polyurethane covered golf balls made from a composition of polyurethane prepolymer and a slow-reacting amine curing agent, and/or a difunctional glycol. The first commercially successful polyurethane covered golf ball was the Titleist® Professional ball, first released in 1993.

Unlike SURLYN® or ionomer-covered golf balls, polyurethane golf ball covers can be formulated to possess the soft "feel" of balata covered golf balls. However, golf ball covers made from polyurethane have not, to date, fully matched SURLYN®-covered golf balls with respect to resilience or the rebound that is a function of the initial velocity of a golf ball after impact with a golf club.

U.S. Pat. No. 3,989,568 discloses a three-component system employing either one or two polyurethane prepolymers and one or two polyols or fast-reacting diamine curing agents. The reactants chosen for the system must have different rates of reactions within two or more competing reactions.

U.S. Pat. No. 4,123,061 discloses a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a fast-reacting diamine curing agent.

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U.S. Pat. No. 5,334,673 discloses a golf ball cover made from a composition of a polyurethane prepolymer and a slow-reacting polyamine curing agent and/or a difunctional glycol. Resultant golf balls are found to have improved shear resistance and cut resistance compared to covers made from balata or SURLYN®

U.S. Pat. No. 5,692,974 discloses methods of using cationic ionomers in golf ball cover compositions Additionally, the patent relates to golf balls having covers and cores incorporating urethane ionomers. Improved resiliency and initial velocity are achieved by the addition of an alkylating agent such as t-butyl-chloride which induces ionic interactions in the polyurethane to produce cationic type ionomers.

International Patent Application WO 98/37929 discloses a composition for golf ball covers that comprises a blend of a diisocyanate/polyol prepolymer and a curing agent comprising a blend of a slow-reacting diamine and a fast-reacting diamine. Improved "feel", playability, and durability characteristics are exhibited.

Conventional polyurethane elastomers are known to have lower resiliency than SURLYN® and other ionomer resins. It has now been discovered that the use of a polyurethane composition, according to the present invention, in forming golf ball cores, intermediate and mantle layers, and/or covers, can raise the velocity of a golf ball prepared with the composition: (1) closer to the velocities observed with SURLYN®-covered golf balls; and (2) higher than the velocities exhibited using alternative urethane compositions Additionally, it is desired to combine polyurethane cover compositions with polybutadiene core materials, especially those having resilience indices greater than about 40. Cores formed of materials such as these have been found to provide exceptional resiliency characteristics without a loss in performance characteristics (i e., decreased compression)

It is thus desired to prepare golf balls having lower compression, i e., a softer ball, while having the same or higher resilience than conventional balls. It is alternatively desired to obtain the same or lower compression while achieving greater resilience.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 200,000 and a resilience index of at least about 40; and a cover layer comprising a polyurethane composition formed from a prepolymer having no greater than 7.5 percent by weight unreacted isocyanate groups Preferably, the resilience index is greater than about 50

The prepolymer may include an isocyanate, at least one polyol, and at least one curing agent. Preferably, the isocyanate includes 4,4'-diphenylmethane diisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-phenylene diisocyanate, toluene diisocyanate, isophoronediisocyanate, p-methylxylene diisocyanate, m-methylxylene diisocyanate, o-methylxylene diisocyanate, or a mixture thereof. The at least one polyol may include polyether polyols, hydroxy-terminated polybutadiene, polyester polyols, polycaprolactone polyols, polycarbonate polyols, and mixtures thereof. The curing agent may include a polyamine curing agent, a polyol curing agent, or a mixture thereof. It is preferred, however, that the curing agent is a polyamine curing agent.

If the polyamine is selected as the curing agent, the polyamine curing agent may include 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-

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diamine and isomers thereof; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino dipbenyl methane; p, p'-methylene dianiline; phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenyl-methane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); and mixtures thereof.

In one embodiment, however, the curing agent is a polyol curing agent. If the curing agent is a polyol, preferably, the polyol curing agent includes ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcino-hydroxyethyl) ether; hydroquinone-di-(β-hydroxyethyl) ether; trimethylol propane, and mixtures thereof

In a another embodiment, the prepolymer has between about 2.5 percent and about 7.5 percent by weight unreacted isocyanate groups. The cover layer preferably has a thickness of less than about 0.05 inches. Further, the center should have a Mooney viscosity of between about 40 and about 80 and, preferably, between about 45 and about 60. In a preferred embodiment, the polybutadiene has a vinyl-polybutadiene isomer content of less than about 2 percent by weight and the polybutadiene has a cis-isomer content of at least about 95 percent by weight.

The golf ball center outer diameter is preferably of no less than about 1.55 inches and, additionally, the center further includes a material formed from a conversion reaction of polybutadiene having a first amount of trans-polybutadiene, a free radical source, and at least one cis-to-trans catalyst. Preferably, the reaction occurs at a temperature sufficient to form a polybutadiene reaction product having an second amount of trans-polybutadiene greater than the first amount of trans-polybutadiene The cis-to-trans catalyst may include at least one of a organosulfur component, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound. The organosulfur component may include at least one of 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido dipbenyl disulfide. Preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 10 parts per hundred of polybutadiene

In another embodiment, the golf ball further includes an intermediate layer juxtaposed between the center and the cover layer, wherein the intermediate layer comprises a material formed from a conversion reaction of polybutadiene having a first amount of trans-polybutadiene, a free radical source, and a cis-to-trans catalyst comprising at least one organosulfur component, wherein the intermediate layer has an outer diameter of no less than about 1.58 inches, and wherein the center has an outer diameter of less than about 1.55 inches. In yet another embodiment, the cover layer comprises an inner cover layer and an outer cover layer, the inner cover layer juxtaposed the center and the outer cover layer. Preferably, at least one of the inner and outer cover layer has a thickness of less than about 0.05 inches.

If present, the inner cover layer is formed from at least one material selected from the group comprising of an ionomer

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resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer, nylon, acrylonitrile butadiene-styrene copolymer or blends thereof. In still another embodiment, the inner cover has an outer diameter of at least about 1.55 inches and, preferably, between about 1.58 and about 1.64 inches. In an additional embodiment, the polyurethane is a thermoplastic or thermoset material.

The present invention is also directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer; and an outer cover layer comprising of a polyurethane composition formed from a prepolymer having no greater than about 7.5 percent by weight unreacted isocyanate groups. Preferably, the resilience index is greater than about 50.

The prepolymer may include an isocyanate, at least one polyol, and at least one curing agent. Preferably, the isocyanate includes 4,4'-diphenylmethane diisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, carbodiimidemodified liquid 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-phenylene diisocyanate, toluene diisocyanate, isophoronediisocyanate, p-methylxylene diisocyanate, m-methylxylene diisocyanate, o-methylxylene diisocyanate, or a mixture thereof. The at least one polyol may include polyether polyols, hydroxyterminated polybutadiene, polyester polyols, polycaprolactone polyols, polycarbonate polyols, and mixtures thereof. The curing agent may include a polyamine curing agent, a polyol curing agent, or a mixture thereof. It is preferred, however, that the curing agent is a polyamine curing agent.

If the polyamine is selected as the curing agent, the polyamine curing agent may include 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline; phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); and mixtures thereof.

In one embodiment, however, the curing agent is a polyol curing agent. If the curing agent is a polyol, preferably, the polyol curing agent includes ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy] benzene; 1,3-bis-{2-[2-(2-hydroxyethoxy)ethoxy] ethoxy} benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(-hydroxyethyl) ether; hydroquinone-di-(-hydroxyethyl)ether; trimethylol propane, and mixtures thereof.

In a another embodiment, the prepolymer has between about 2.5 percent and about 7.5 percent by weight unreacted isocyanate groups. At least one of the inner and outer cover layers preferably has a thickness of less than about 0.05 inches. Further, the center should have a Mooney viscosity of between about 40 and about 80. In a preferred

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embodiment, the polybutadiene has a vinyl-polybutadiene isomer content of less than about 2 percent by weight and the polybutadiene has a cis-isomer content of at least about 95 percent by weight.

The golf ball center outer diameter is preferably of no less than about 1.55 inches and, additionally, the center further includes a material formed from a conversion reaction of polybutadiene having a first amount of trans-polybutadiene, a free radical source, and at least one cis-to-trans catalyst. Preferably, the reaction occurs at a temperature sufficient to form a polybutadiene reaction product having an second amount of trans-polybutadiene greater than the first amount of trans-polybutadiene. The cis-to-trans catalyst may include at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound. The organosulfur component may include at least one of 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide. Preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 10 parts per hundred of polybutadiene.

In one embodiment, the inner cover layer includes an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer or blends thereof. The inner cover may have an outer diameter of at least about 1.55 inches and, preferably, between about 1.58 and about 1.64 inches. In an additional embodiment, the polyurethane is a thermoplastic or thermoset material.

The present invention is also directed to a golf ball comprising a center formed of a cis-polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer, the inner cover layer comprising a polyurethane; and an outer cover layer comprising an ionomer or an elastomeric material.

The present invention is also directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer; and an outer cover layer; wherein the inner and outer cover layers are formed of a polyurethane composition.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a two-piece golf ball having a cover and a core according to the invention;

FIG. 2 is a cross-section of a golf ball having an intermediate layer between a cover and a center according to the invention;

FIG. 3 is a cross-section of a golf ball having more than one intermediate layer between a cover and a center according to the invention.

DEFINITIONS

The term "about," as used herein in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

As used herein, "cis-to-trans catalyst" means any component or a combination thereof that will convert at least a

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portion of cis-polybutadiene isomer to trans-polybutadiene isomer at a given temperature It should be understood that the combination of the cis-isomer, the trans-isomer, and any vinyl-isomer, measured at any given time, comprises 100 percent of the polybutadiene.

As used herein, the term "active ingredients" is defined as the specific components of a mixture or blend that are essential to the chemical reaction.

As used herein, substituted and unsubstituted "aryl" groups means a hydrocarbon ring bearing a system of conjugated double bonds, typically comprising $4n+2\pi$ ring electrons, where n is an integer. Examples of aryl groups include, but are not limited to phenyl, naphthyl, anisyl, tolyl, xylenyl and the like. According to the present invention, aryl also includes heteroaryl groups, e g., pyrimidine or thiophene. These aryl groups may also be substituted with any number of a variety of functional groups In addition to the functional groups described herein in connection with carbocyclic groups, functional groups on the aryl groups can include hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfona-mide; and phosphates and phosphites; and a combination thereof.

As used herein, the term "Atti compression" is defined as the deflection of an object or material relative to the deflec-tion of a calibrated spring, as measured with an Atti Com-pression Gauge, that is commercially available from Atti Engineering Corp. of Union City, N.J. Atti compression is typically used to measure the compression of a golf ball. When the Atti Gauge is used to measure cores having a diameter of less than 1.680 inches, it should be understood that a metallic or other suitable shim is used to make the measured object 1.680 inches in diameter However, when referring to the compression of a core, it is preferred to use a compressive load measurement. The term "compressive load" is defined as the normalized load in pounds for a 10.8-percent diametrical deflection for a spherical object having a diameter of 1.58 inches.

As used herein, substituted and unsubstituted "carbocy-clic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such func-tional groups include those described above, and lower alkyl groups having from 1–28 carbon atoms The cyclic groups of the invention may further comprise a heteroatom.

As used herein, the term "coefficient of restitution" for golf balls is defined as the ratio of the rebound velocity to the inbound velocity when balls are fired into a rigid plate. The inbound velocity is understood to be 125 ft/s

As used herein, the term "dynamic stiffness" is defined as load divided by the deflection for a 1 4-mm spherical radius penetration probe oscillating at 1 Hz with an amplitude of 100 μm. The probe dynamically penetrates the surface of a sample material. Material samples of spherical cores were prepared by sectioning out a 6-mm-thick layer along the equator of core to produce a disk 6 mm thick with one surface containing the geometric center of the core. By positioning the probe at any selected radial position on the disk, a dynamic stiffness measurement may be obtained. Accurate dynamic measurements may be made by keeping the material sample at a substantially uniform temperature. The dynamic stiffness was acquired using a Dynamic

Mechanical Analyzer, Model DMA 2980 available from TA Instruments Corporation of New Castle, Del. The instrument setting for the DMA 2980 were 1-Hz frequency, 100-μm amplitude, 0 3-N static load, and auto strain of 105 percent. The 1.4-mm spherical radius probe is available from TA Instruments as a penetration kit accessory to the DMA 2980. The DMA 2980 is equipped with a temperature-controlled chamber that enables testing at a wide variety of ambient temperatures.

The method and instrument utilized for measuring "dynamic stiffness" may also be used to measure loss tangent (also commonly referred to as tan δ). Loss tangent is the ratio of loss modulus to storage modulus. Loss modulus is the portion of modulus which is out of phase with displacement and storage modulus is the portion of modulus which is in phase with displacement. The DMA 2980 automatically calculates and reports loss tangent.

As used herein, the terms "Group VIA component" or "Group VIA element" mean a component that includes a sulfur component, a selenium component, or a tellurium component, or a combination thereof.

As used herein, the term "sulfur component" means a component that is elemental sulfur, polymeric sulfur, or a combination thereof It should be further understood that "elemental sulfur" refers to the ring structure of S_8 and that "polymeric sulfur" is a structure including at least one additional sulfur relative to the elemental sulfur.

As used herein, the term "fluid" includes a liquid, a paste, a gel, a gas, or any combination thereof.

As used herein, the term "molecular weight" is defined as the absolute weight average molecular weight. The molecu-lar weight is determined by the following method: approxi-mately 20 mg of polymer is dissolved in 10 mL of tetrahy-drofuran ("THF"), which may take a few days at room temperature depending on the polymer's molecular weight and distribution One liter of THF is filtered and degassed before being placed in a high-performance liquid chroma-tography ("HPLC") reservoir The flow rate of the HPLC is set to 1 mL/min through a Viscogel column. This non-shedding, mixed bed, column model GMH$_{HR}$-H, which has an ID of 7.8 mm and 300 mm long is available from Viscotek Corp of Houston, Tex. The THF flow rate is set to 1 mL/min for at least one hour before sample analysis is begun or until stable detector baselines are achieved During this purging of the column and detector, the internal tem-perature of the Viscotek TDA Model 300 triple detector should be set to 40° C. This detector is also available from Viscotek Corp. The three detectors (i e., Refractive Index, Differential Pressure, and Light Scattering) and the column should be brought to thermal equilibrium, and the detectors should be purged and zeroed, to prepare the system for calibration according to the instructions provided with this equipment. A 100-μL aliquot of sample solution can then be injected into the equipment and the molecular weight of each sample can be calculated with the Viscotek's triple detector software. When the molecular weight of the polyb-utadiene material is measured, a dn/dc of 0.130 should always be used It should be understood that this equipment and these methods provide the molecular weight numbers described and claimed herein, and that other equipment or methods will not necessarily provide equivalent values as used herein.

As used herein, the term "multilayer" means at least two layers and includes liquid center balls, wound balls, hollow-center balls, and balls with at least two intermediate layers and/or an inner or outer cover.

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As used herein, the term "parts per hundred," also known as "phr," is defined as the number of parts by weight of a particular component present in a mixture, relative to 100 parts by weight of the total polymer component. Mathematically, this can be expressed as the weight of an ingredient divided by the total weight of the polymer, multiplied by a factor of 100.

As used herein, the term "substantially free" means less than about 5 weight percent, preferably less than about 3 weight percent, more preferably less than about 1 weight percent, and most preferably less than about 0.01 weight percent.

As used herein the term "resilience index" is defined as the difference in loss tangent measured at 10 cpm and 1000 cpm divided by 990 (the frequency span) multiplied by 100,000 (for normalization and unit convenience). The loss tangent is measured using an RPA 2000 manufactured by Alpha Technologies of Akron, Ohio. The RPA 2000 is set to sweep from 2.5 to 1000 cpm at a temperature of 100° C. using an arc of 0.5 degrees. An average of six loss tangent measurements were acquired at each frequency and the average is used in calculation of the resilience index. The computation of resilience index is as follows:

$$\text{Resilience Index} = 100,000 \cdot [(\text{loss tangent@10 } cpm) - (\text{loss tangent@1000 } cpm)]/990$$

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, a golf ball 10 of the present invention can include a core 12, a cover 16, and optional inner cover layer 16a surrounding the core 12. Referring to FIG. 2, a golf ball 20 of the present invention can include a center 22, a cover 26, an inner cover layer 26a, and at least one intermediate layer 24 disposed between the cover and the center. Each of the cover and center may also include more than one layer; i.e., the golf ball can be a conventional three-piece wound ball, a two-piece ball, a ball having a multi-layer core or an intermediate layer or layers, etc. Thus, referring to FIG. 3, a golf ball 30 of the present invention can include a center 32, a cover 38, and intermediate layers 34 and 36 disposed between the cover and the center. Although FIG. 3 shows only two intermediate layers, it will be appreciated that any number or type of intermediate layers may be used, as desired.

The present invention relates to two piece golf balls having a core and a cover, or multilayer golf balls having a solid, hollow, or fluid-filled center, a cover, and at least one intermediate layer disposed concentrically adjacent to the center. At least one of the center or optional intermediate layer includes a reaction product that includes a cis-to-trans catalyst, a resilient polymer component having polybutadiene, a free radical source, and optionally, a crosslinking agent, a filler, or both. Preferably, the reaction product has a first dynamic stiffness measured at −50° C. that is less than about 130 percent of a second dynamic stiffness measured at 0° C. More preferably, the first dynamic stiffness is less than about 125 percent of the second dynamic stiffness. Most preferably, the first dynamic stiffness is less than about 110 percent of the second dynamic stiffness.

The invention also includes a method to convert the cis-isomer of the polybutadiene resilient polymer component to the trans-isomer during a molding cycle and to form a golf ball. Various combinations of polymers, cis-to-trans catalysts, fillers, crosslinkers, and a source of free radicals, may be used. To obtain a higher resilience and lower

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compression center or intermediate layer, a high-molecular weight polybutadiene with a cis-isomer content preferably greater than about 90 percent is converted to increase the percentage of trans-isomer content at any point in the golf ball or portion thereof, preferably to increase the percentage throughout substantially all of the golf ball or portion thereof, during the molding cycle. More preferably, the cis-polybutadiene isomer is present in an amount of greater than about 95 percent of the total polybutadiene content. Without wishing to be bound by any particular theory, it is believed that a low amount of 1,2-polybutadiene isomer ("vinyl-polybutadiene") is desired in the initial polybutadiene, and the reaction product. Typically, the vinyl polybutadiene isomer content is less than about 7 percent. Preferably, the vinyl polybutadiene isomer content is less than about 4 percent. More preferably, the vinyl polybutadiene isomer content is less than about 2 percent. Without wishing to be bound by any particular theory, it is also believed that the resulting mobility of the combined cis- and trans-polybutadiene backbone is responsible for the lower modulus and higher resilience of the reaction product and golf balls including the same.

To produce a polymer reaction product that exhibits the higher resilience and lower modulus (low compression) properties that are desirable and beneficial to golf ball playing characteristics, high-molecular-weight cis-1,4-polybutadiene, preferably may be converted to the trans-isomer during the molding cycle. The polybutadiene material typically has a molecular weight of greater than about 200,000. Preferably, the polybutadiene molecular weight is greater than about 250,000, more preferably between about 300,000 and 500,000. Without wishing to be bound by any particular theory, it is believed that the cis-to-trans catalyst component, in conjunction with the free radical source, acts to convert a percentage of the polybutadiene polymer component from the cis- to the trans-conformation. The cis-to-trans conversion requires the presence of a cis-to-trans catalyst, such as an organosulfur or metal-containing organosulfur compound, a substituted or unsubstituted aromatic organic compound that does not contain sulfur or metal, an inorganic sulfide compound, an aromatic organometallic compound, or mixtures thereof. The cis-to-trans catalyst component may include one or more of the other cis-to-trans catalysts described herein.

In one embodiment, the at least one organosulfur component is substantially free of metal, which typically means less than about 10 weight percent metal, preferably less than about 3 weight percent metal, more preferably less than about 1 weight percent metal, and most preferably only trace amounts of metal, such as less than about 0.01 weight percent.

As used herein when referring to the invention, the term "organosulfur compound(s)" or "organosulfur component(s)," means at least one of 4,4'-diphenyl disulfide; 4,4'-ditolyl disulfide; 2,2'-benzamido diphenyl disulfide; bis (2-aminophenyl)disulfide; bis(4-aminophenyl)disulfide; bis (3-aminophenyl)disulfide; 2,2'-bis(4-aminonaphthyl) disulfide; 2,2'-bis(3-aminonaphthyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(5-aminonaphthyl) disulfide; 2,2'-bis(6-aminonaphthyl)disulfide; 2,2'-bis(7-aminonaphthyl)disulfide; 2,2'-bis(8-aminonaphthyl) disulfide; 1,1'-bis(2-aminonaphthyl)disulfide; 1,1'-bis(3-aminonaphthyl)disulfide; 1,1'-bis(3-aminonaphthyl) disulfide; 1,1'-bis(4-aminonaphthyl)disulfide; 1,1'-bis(5-aminonaphthyl)disulfide; 1,1'-bis(6-aminonaphthyl) disulfide; 1,1'-bis(7-aminonaphthyl)disulfide; 1,1'-bis(8-aminonaphthyl)disulfide; 1,2'-diamino-1,2'-

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dithiodinaphthalene; 2,3'-diamino-1,2'-dithiodinaphthalene; bis(4-chlorophenyl)disulfide; bis(2-chlorophenyl)disulfide; bis(3-chlorophenyl)disulfide; bis(4-bromophenyl)disulfide; bis(2-bromophenyl)disulfide; bis(3-bromophenyl)disulfide; bis(4-fluorophenyl)disulfide; bis(4-iodophenyl)disulfide; bis (2,5-dichlorophenyl)disulfide; bis(3,5-dichlorophenyl) disulfide; bis(2,4-dichlorophenyl)disulfide; bis(2,6-dichlorophenyl)disulfide; bis(2,5-dibromophenyl)disulfide; bis(3,5-dibromophenyl)disulfide; bis(2-chloro-5-bromophenyl)disulfide; bis(2,4,6-trichlorophenyl)disulfide; bis(2,3,4,5,6-pentachlorophenyl)disulfide; bis(4-cyanophenyl)disulfide; bis(2-cyanophenyl)disulfide; bis(4-nitrophenyl)disulfide; bis(2-nitrophenyl)disulfide; 2,2'-dithiobenzoic acid ethylester; 2,2'-dithiobenzoic acid methylester; 2,2'-dithiobenzoic acid; 4,4'-dithiobenzoic acid ethylester; bis(4-acetylphenyl)disulfide; bis(2-acetylphenyl) disulfide; bis(4-formylphenyl)disulfide; bis(4-carbamoylphenyl)disulfide; 1,1'-dinaphthyl disulfide; 2,2'-dinaphthyl disulfide; 1,2'-dinaphthyl disulfide; 2,2'-bis(1-chlorodinaphthyl)disulfide; 2,2'-bis(1-bromonaphthyl) disulfide; 1,1'-bis(2-chloronaphthyl)disulfide; 2,2'-bis(1-cyanonaphtyl)disulfide; 2,2'-bis(1-acetylnaphthyl)disulfide; and the like; or a mixture thereof. Preferred organosulfur components include 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide, or a mixture thereof. A more preferred organosulfur component includes 4,4'-ditolyl disulfide. The organosulfur cis-to-trans catalyst, when present, is preferably present in an amount sufficient to produce the reaction product so as to contain at least about 12 percent trans-polybutadiene isomer, but typically is greater than about 32 percent trans-polybutadiene isomer based on the total resilient polymer component. Suitable metal-containing organosulfur components include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethyldithiocarbamate, diamyldithiocarbamate, and dimethyldithiocarbamate, or mixtures thereof. Suitable substituted or unsubstituted aromatic organic components that do not include sulfur or a metal include, but are not limited to, 4,4'-diphenyl acetylene, azobenzene, or a mixture thereof. The aromatic organic group preferably ranges in size from C_6 to C_{20}, and more preferably from C_6 to C_{10}. Suitable inorganic sulfide components include, but are not limited to titanium sulfide, manganese sulfide, and sulfide analogs of iron, calcium, cobalt, molybdenum, tungsten, copper, selenium, yttrium, zinc, tin, and bismuth. The cis-to-trans catalyst may also be a blend of an organosulfur component and an inorganic sulfide component.

A substituted or unsubstituted aromatic organic compound may also be included in the cis-to-trans catalyst. In one embodiment, the aromatic organic compound is substantially free of metal. Suitable substituted or unsubstituted aromatic organic components include, but are not limited to, components having the formula $(R_1)_x$-R_3-M-R_4-$(R_2)_y$, wherein R_1 and R_2 are each hydrogen or a substituted or unsubstituted C_{1-20} linear, branched, or cyclic alkyl, alkoxy, or alkylthio group, or a single, multiple, or fused ring C_6 to C_{24} aromatic group; x and y are each an integer from 0 to 5; R_3 and R4 are each selected from a single, multiple, or fused ring C_6 to C_{24} aromatic group; and M includes an azo group or a metal component. R_3 and R_4 are each preferably selected from a C_6 to C_{10} aromatic group, more preferably selected from phenyl, benzyl, naphthyl, benzamido, and benzothiazyl. R_1 and R_2 are each preferably selected from a substituted or unsubstituted C_{1-10} linear, branched, or cyclic alkyl, alkoxy, or alkylthio group or a C_6 to C_{10} aromatic group. When R_1, R_2, R_3, or R_4, are substituted, the substitution may include one or more of the following substituent

groups: hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites. When M is a metal component, it may be any suitable elemental metal available to those of ordinary skill in the art. Typically, the metal will be a transition metal, although preferably it is tellurium or selenium.

The cis-to-trans catalyst can also include a Group VIA component, as defined herein. Elemental sulfur and polymeric sulfur are commercially available from, e.g., Elastochem, Inc. of Chardon, Ohio. Exemplary sulfur catalyst compounds include PB(RM-S)-80 elemental sulfur and PB(CRST)-65 polymeric sulfur, each of which is available from Elastochem, Inc. An exemplary tellurium catalyst under the tradename TELLOY and an exemplary selenium catalyst under the tradename VANDEX are each commercially available from RT Vanderbilt.

The cis-to-trans catalyst is preferably present in an amount from about 0.1 to 10 parts per hundred of the total resilient polymer component. More preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 5 parts per hundred of the total resilient polymer component. Most preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 8 parts per hundred of the total resilient polymer component. The cis-to-trans catalyst is typically present in an amount sufficient to produce the reaction product so as to increase the trans-polybutadiene isomer content to contain from about 5 percent to 70 percent trans-polybutadiene based on the total resilient polymer component.

The measurement of trans-isomer content of polybutadiene referred to herein was and can be accomplished as follows. Calibration standards are prepared using at least two polybutadiene rubber samples of known trans-content, e.g., high and low percent trans-polybutadiene). These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5% to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally spaced points.

Using a commercially available Fourier Transform Infrared ("FTIR") spectrometer equipped with a Photoacoustic ("PAS") cell, a PAS spectrum of each standard was obtained using the following instrument parameters: scan at speed of 2.5 KHz (0.16 cm/s optical velocity), use a 1.2 KHz electronic filter, set an undersampling ratio of 2 (number of laser signal zero crossings before collecting a sample), co-add a minimum of 128 scans at a resolution of 4 cm^{-1} over a range of 375 to 4000 cm^{-1} with a sensitivity setting of 1.

The cis-, trans-, and vinyl-polybutadiene peaks are typically found between 600 and 1100 cm^{-1} in the PAS spectrum. The area under each of the trans-polybutadiene peaks can be integrated. Determining the fraction of each peak area relative to the total area of the three isomer peaks allow construction of a calibration curve of the trans-polybutadiene area fraction versus the actual trans-polybutadiene content. The correlation coefficient (R^2) of the resulting calibration curve must be a minimum of 0.95.

A PAS spectrum is obtained, using the parameters described above, for the unknown core material at the point of interest (e.g., the surface or center of the core) by filling the PAS cell with a sample containing a freshly cut, uncontaminated surface free of foreign matters, such as mold release and the like. The trans-polybutadiene area fraction of

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the unknown is analyzed to determine the actual trans-isomer content from the calibration curve.

In one known circumstance when barium sulfate is included, the above method for testing trans-content may be less accurate. Thus, an additional or alternative test of the trans-content of polybutadiene is as follows. Calibration standards are prepared using at least two polybutadienes of known trans-content (e.g., high and low percent trans-polybutadiene). These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5% to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally spaced points.

Using a Fourier Transform Raman ("FT-Raman") spectrometer equipped with a near-infrared laser, a Stokes Raman spectrum should be obtained from each standard using the following instrument parameters: sufficient laser power to obtain a good signal-to-noise ratio ("S/N") without causing excessive heating or fluorescence (typically about 400 to 800 mW is suitable); a resolution of 2 cm^{-1}; over a Raman shift spectral range of about 400 to 4000 cm^{-1}; and co-adding at least 300 scans.

A calibration curve may be constructed from the data generated above, using a chemometrics approach and software such as PLSplus/IQ from Galactic Industries Corp. of Salem, NE. An acceptable calibration was obtained with this software using a PLS-1 curve generated using an SNV (detrend) pathlength correction, a mean center data preparation, and a 5-point SG second derivative over the spectral range from about 1600 to 1700 cm^{-1}. The correlation coefficient (R^2) of the resulting calibration curve must be a minimum of 0.95.

A Raman spectrum of the core material is obtained using this instrument at the point of interest in the sample (e.g., surface or center of the golf ball core). The sample must be free of foreign matter, such as mold release, etc. Analyze the spectrum of the sample using the PLS calibration curve to determine trans-polybutadiene isomer content of the sample.

A free-radical source, often alternatively referred to as a free-radical initiator, is required in the composition and method. The free-radical source is typically a peroxide, and preferably an organic peroxide. Suitable free-radical sources include di-t-amyl peroxide, di(2-t-butyl-peroxyisopropyl) benzene peroxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, di-t-butyl peroxide, 2,5-di-(t-butylperoxy)-2,5-dimethyl hexane, n-butyl-4,4-bis(t-butylperoxy)valerate, lauryl peroxide, benzoyl peroxide, t-butyl hydroperoxide, and the like, and any mixture thereof. The peroxide is typically present in an amount greater than about 0.1 parts per hundred of the total resilient polymer component, preferably about 0.1 to 15 parts per hundred of the resilient polymer component, and more preferably about 0.2 to 5 parts per hundred of the total resilient polymer component. It should be understood by those of ordinary skill in the art that the presence of certain cis-to-trans catalysts according to the invention may require a larger amount of free-radical source, such as the amounts described herein, compared to conventional cross-linking reactions. The free radical source may alternatively or additionally be one or more of an electron beam, UV or gamma radiation, x-rays, or any other high energy radiation source capable of generating free radicals. It should be further understood that heat often facilitates initiation of the generation of free radicals.

Crosslinkers are included to increase the hardness of the reaction product. Suitable crosslinking agents include one or

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more metallic salts of unsaturated fatty acids or monocarboxylic acids, such as zinc, calcium, or magnesium acrylate salts, and the like, and mixtures thereof. Preferred acrylates include zinc acrylate, zinc diacrylate, zinc methacrylate, and zinc dimethacrylate, and mixtures thereof. The crosslinking agent must be present in an amount sufficient to crosslink a portion of the chains of polymers in the resilient polymer component. For example, the desired compression may be obtained by adjusting the amount of crosslinking. This may be achieved, for example, by altering the type and amount of crosslinking agent, a method well-known to those of ordinary skill in the art. The crosslinking agent is typically present in an amount greater than about 0.1 percent of the resilient polymer component, preferably from about 10 to 40 percent of the resilient polymer component, more preferably from about 10 to 30 percent of the resilient polymer component. When an organosulfur is selected as the cis-to-trans catalyst, zinc diacrylate may be selected as the crosslinking agent and is present in an amount of less than about 25 phr.

Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, the specific gravity (i.e., density-modifying fillers), the modulus, the tear strength, reinforcement, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls, e.g., a lower weight ball is preferred for a player having a low swing speed.

The polymers, free-radical initiator, filler(s), and any other materials used in forming either the golf ball center or any portion of the core, in accordance with invention, may be combined to form a mixture by any type of mixing known to one of ordinary skill in the art. Suitable types of mixing include single pass and multi-pass mixing, and the like. The crosslinking agent, and any other optional additives used to modify the characteristics of the golf ball center or additional layer(s), may similarly be combined by any type of mixing. A single-pass mixing process where ingredients are added sequentially is preferred, as this type of mixing tends to increase efficiency and reduce costs for the process. The preferred mixing cycle is single step wherein the polymer, cis-trans catalyst, filler, zinc diacrylate, and peroxide are added sequentially. Suitable mixing equipment is well known to those of ordinary skill in the art, and such equipment may include a Banbury mixer, a two-roll mill, or a twin screw extruder. Conventional mixing speeds for combining polymers are typically used, although the speed must be high enough to impart substantially uniform dispersion of the constituents. On the other hand, the speed should not be too high, as high mixing speeds tend to break down the polymers being mixed and particularly may undesirably decrease the molecular weight of the resilient polymer component. The speed should thus be low enough to avoid high shear, which may result in loss of desirably high molecular weight portions of the polymer component. Also, too high a mixing speed may undesirably result in creation

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of enough heat to initiate the crosslinking before the pre-forms are shaped and assembled around a core. The mixing temperature depends upon the type of polymer components, and more importantly, on the type of free-radical initiator. For example, when using di(2-t-butyl-peroxyisopropyl) benzene as the free-radical initiator, a mixing temperature of about 80° C. to 125° C., preferably about 88° C. to 110° C., and more preferably about 90° C. to 100° C. is suitable to safely mix the ingredients. Additionally, it is important to maintain a mixing temperature below the peroxide decomposition temperature. For example, if dicumyl peroxide is selected as the peroxide, the temperature should not exceed 200° F. Suitable mixing speeds and temperatures are well-known to those of ordinary skill in the art, or may be readily determined without undue experimentation.

The mixture can be subjected to, e.g., a compression or injection molding process, to obtain solid spheres for the center or hemispherical shells for forming an intermediate layer. The polymer mixture is subjected to a molding cycle in which heat and pressure are applied while the mixture is confined within a mold. The cavity shape depends on the portion of the golf ball being formed. The compression and heat liberates free radicals by decomposing one or more peroxides, which may initiate the cis-to-trans conversion and crosslinking simultaneously. The temperature and duration of the molding cycle are selected based upon the type of peroxide and cis-trans catalyst selected. The molding cycle may have a single step of molding the mixture at a single temperature for a fixed time duration. An example of a single step molding cycle, for a mixture that contains dicumyl peroxide, would hold the polymer mixture at 340° F. for a duration of 15 minutes. The molding cycle may also include a two-step process, in which the polymer mixture is held in the mold at an initial temperature for an initial duration of time, followed by holding at a second, typically higher temperature for a second duration of time. An example of a two-step molding cycle would be holding the mold at 290° F. for 40 minutes, then ramping the mold to 340° F. where it is held for a duration of 20 minutes. In a preferred embodiment of the current invention, a single-step cure cycle is employed. Single-step processes are effective and efficient, reducing the time and cost of a two-step process. The resilient polymer component, polybutadiene, cis-to-trans conversion catalyst, additional polymers, free-radical initiator, filler, and any other materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a golf ball by an injection molding process, which is also well-known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, a particularly suitable curing time is about 5 to 18 minutes, preferably from about 8 to 15 minutes, and more preferably from about 10 to 12 minutes. Those of ordinary skill in the art will be readily able to adjust the curing time upward or downward based on the particular materials used and the discussion herein.

The cured resilient polymer component, which contains a greater amount of trans-polybutadiene than the uncured resilient polymer component, is formed into an article having a first hardness at a point in the interior and a surface having a second hardness such that the second hardness differs from the first hardness by greater than 10 percent of the first hardness. Preferably, the article is a sphere and the point is the midpoint of the article. In another embodiment, the second hardness differs from the first by greater than 20 percent of the first hardness. The cured article also has a first amount of trans-polybutadiene at an interior location and a

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second amount of trans-polybutadiene at a surface location, wherein the first amount is at least about 6 percent less than the second amount, preferably at least about 10 percent less than the second amount, and more preferably at least about 20 percent less than the second amount. The interior location is preferably a midpoint and the article is preferably a sphere. The compression of the core, or portion of the core, of golf balls prepared according to the invention is preferably below about 50, more preferably below about 25.

The cover provides the interface between the ball and a club. Properties that are desirable for the cover are good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release, among others. The cover typically has a thickness to provide sufficient strength, good performance characteristics and durability. The cover preferably has a thickness of less than about 0.1 inches, more preferably, less than about 0.05 inches, and most preferably, between about 0.02 and about 0.04 inches. The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer, and an outer cover layer. In this embodiment, preferably, at least one of the inner and outer cover layers has a thickness of less than about 0.05 inches, more preferably between about 0.02 and about 0.04 inches. Most preferably, the thickness of either layer is about 0.03 inches.

When the golf ball of the present invention includes an intermediate layer, such as an inner cover layer, this layer can include any materials known to those of ordinary skill in the art, including thermoplastic and thermosetting materials, but preferably the intermediate layer can include any suitable materials, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN of E. I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEK or ESCOR of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric intermediate materials, such as:

(1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;

(2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;

(3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U.S. Pat. No. 5,334,673;

(4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;

(5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly (caprolactam), and blends of polyamides with

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<table>
<tr><td>19</td><td>20</td></tr>
</table>

SURLYN, polyethylene, ethylene copolymers, ethyl-propylene-non-conjugated diene terpolymer, and the like;

(6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;

(7) Thermoplastics, such as urethanes; olefinic thermo-plastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber, or copoly(ether-amide), such as PEBAX, sold by ELF Atochem of Philadelphia, Pa.;

(8) Polyphenylene oxide resins or blends of polyphe-nylene oxide with high impact polystyrene as sold under the trademark NORYL by General Electric Com-pany of Pittsfield, Mass.;

(9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL by E. I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD by General Electric Company of Pittsfield, Mass.;

(10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadi-ene styrene or ethylene vinyl acetate or other elas-tomers; and

(11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the optional intermediate layer includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethelyne vinyl alcohol), poly(tetrafluoroethylene) and their copoly-mers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. More preferably, in a low spin rate embodiment designed for maximum distance, the acrylic or methacrylic acid is present in about 15 to 35 weight percent, making the ionomer a high modulus ionomer. In a high spin embodiment, the cover includes an ionomer where an acid is present in about 10 to 15 weight percent and includes a softening comonomer.

The cover preferably include a polyurethane composition comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent.

Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exem-plary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"), polymeric MDI,

carbodiimide-modified liquid MDI, 4,4'-dicyclohexylmethane diisocyanate ("HH$_{12}$MDI"), p-phenylene diisocyanate ("PPDI"), toluene diisocyanate ("TDI"), 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"), isophoronediisocyanate ("IPDI"), hexamethyl-ene diisocyanate ("HDI"), naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); para-tetramethylxylene diisocyanate ("p-TMXDI"); meta-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diiso-cyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"), tetracene diisocyanate, napthalene diisocyanate, anthracene diisocyanate, and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-, tri-, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, more preferably, between about 2.5% and about 7.5%, and most preferably, between about 4% to about 6.5%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolac-tone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol, more preferably those polyols that have the generic structure:
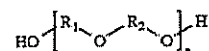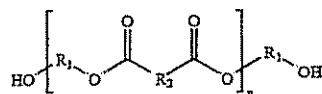
$$HO \left[\begin{array}{c} R_1 \\ \diagdown \diagup \end{array} O \begin{array}{c} R_2 \\ \diagup \diagdown \end{array} O \right]_n H$$

where R_1 and R_2 are straight or branched hydrocarbon chains, each containing from 1 to about 20 carbon atoms, and n ranges from 1 to about 45. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubsti-tuted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

In another embodiment, polyester polyols are included in the polyurethane material of the invention. Preferred poly-ester polyols have the generic structure:
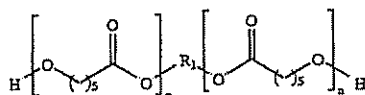
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where R_1 and R_2 are straight or branched hydrocarbon chains, each containing from 1 to about 20 carbon atoms, and n ranges from 1 to about 25. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol, polybutylene adipate glycol, polyethylene propylene adipate glycol, ortho-phthalate-1,6-hexanediol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In another embodiment, polycaprolactone polyols are included in the materials of the invention. Preferably, any polycaprolactone polyols have the generic structure:

where R_1 is a straight chain or branched hydrocarbon chain containing from 1 to about 20 carbon atoms, and n is the chain length and ranges from 1 to about 20. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, the polycarbonate polyols are included in the polyurethane material of the invention. Preferably, any polycarbonate polyols have the generic structure:
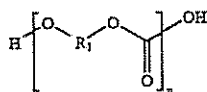
where R_1 is predominantly bisphenol A units -(p-C_6H_4)— $C(CH_3)_2$-(p-C_6H_4)— or derivatives thereof, and n is the chain length and ranges from 1 to about 20. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-

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methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2, 6-diethylaniline); trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

Other suitable polyamine curatives include those having the general formula:
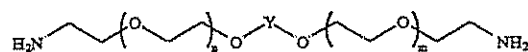
where n and m each separately have values of 0, 1, 2, or 3, and where Y is 1,2-cyclohexyl, 1,3-cyclohexyl, 1,4-cyclohexyl, ortho-phenylene, meta-phenylene, orpara-phenylene, or a combination thereof. Preferably, n and m, each separately, have values of 0, 1, or 2, and preferably, 1 or 2.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy]benzene; 1,3-bis-{2-[2-(2-hydroxyethoxy)ethoxy] ethoxy}benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl)ether; hydroquinone-di-(β-hydroxyethyl)ether; and mixtures thereof. Preferred hydroxy-terminated curatives include ethylene glycol; diethylene glycol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; trimethylol propane, and mixtures thereof.

Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art. Other suitable hydroxy-terminated curatives have the following general chemical structure:
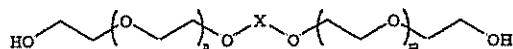
where n and m each separately have values of 0, 1, 2, or 3, and where X is ortho-phenylene, meta-phenylene, para-phenylene, 1,2-cyclohexyl, 1,3-cyclohexyl, or 1,4-cyclohexyl, or mixtures thereof. Preferably, n and m each separately have values of 0, 1, or 2, and more preferably, 1 or 2.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

Any method known to one of ordinary skill in the art may be used to combine the polyisocyanate, polyol, and curing

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agent of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogenous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition.

An optional filler component may be chosen to impart additional density to blends of the previously described components. The selection of such filler(s) is dependent upon the type of golf ball desired (i.e., one-piece, two-piece multi-component, or wound). Examples of useful fillers include zinc oxide, barium sulfate, calcium oxide, calcium carbonate and silica, as well as the other well known corresponding salts and oxides thereof. Additives, such as nanoparticles, glass spheres, and various metals, such as titanium and tungsten, can be added to the polyurethane compositions of the present invention, in amounts as needed, for their well-known purposes. Additional components which can be added to the polyurethane composition include UV stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Due to the very thin nature, it has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the inner core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733, 428, filed May 2, 1995 entitled "Method And Apparatus For Forming Polyurethane Cover On A Golf Ball", the disclosure of which is hereby incorporated by reference in its entirety in the present application.

The cover is preferably formed around the coated core by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using pins moving into holes in each mold. After the reacting materials have resided in top mold halves for about 50 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity.

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A ball cup holds the ball core through reduced pressure (or partial vacuum) in hose. Upon location of the coated core in the halves of the mold after gelling for about 50 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 to Brown et al. and U.S. Pat. No. 5,334,673 to Wu both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

Depending on the desired properties, balls prepared according to the invention can exhibit substantially the same or higher resilience, or coefficient of restitution ("COR"), with a decrease in compression or modulus, compared to balls of conventional construction. Additionally, balls prepared according to the invention can also exhibit substantially higher resilience, or COR, without an increase in compression, compared to balls of conventional construction. Another measure of this resilience is the "loss tangent," or tan δ, which is obtained when measuring the dynamic stiffness of an object. Loss tangent and terminology relating to such dynamic properties is typically described according to ASTM D4092-90. Thus, a lower loss tangent indicates a higher resiliency, thereby indicating a higher rebound capacity. Low loss tangent indicates that most of the energy imparted to a golf ball from the club is converted to dynamic energy, i.e., launch velocity and resulting longer distance. The rigidity or compressive stiffness of a golf ball may be measured, for example, by the dynamic stiffness. A higher dynamic stiffness indicates a higher compressive stiffness. To produce golf balls having a desirable compressive stiffness, the dynamic stiffness of the crosslinked reaction product material should be less than about 50,000 N/m at –50° C. Preferably, the dynamic stiffness should be between about 10,000 and 40,000 N/m at –50° C., more preferably, the dynamic stiffness should be between about 20,000 and 30,000 N/m at –50° C.

The dynamic stiffness is similar in some ways to dynamic modulus. Dynamic stiffness is dependent on probe geometry as described herein, whereas dynamic modulus is a unique material property, independent of geometry. The dynamic stiffness measurement has the unique attribute of enabling quantitative measurement of dynamic modulus and exact measurement of loss tangent at discrete points within a sample article. In the case of this invention, the article is a golf ball core. The polybutadiene reaction product preferably has a loss tangent below about 0.1 at –50° C., and more preferably below about 0.07 at –50° C.

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression (which has been referred to as PGA compression in the past) of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball polybutadiene material of the present invention typically has a flexural modulus of from about 500 psi to 300,000 psi, preferably from about 2000 to 200,000 psi. The golf ball polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D,

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more preferably between about 50 Shore A and 60 Shore D. The specific gravity is typically greater than about 0.7, preferably greater than about 1, for the golf ball polybutadiene material.

The center composition should comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50. A comparison of a number of polybutadiene polymers are listed in Table 1 below. Polymers that produce resilient golf balls and, therefore, are suitable for the present invention, include but are not limited to CB23, CB22, BR60, and 1207G. To clarify the method of computation for resilience index, the resilience index for CB23, for example, is computed as follows:

Resilience Index for CB23=100,000 [(0.954)-(0.407)]/990 Resilience Index for CB23=55

TABLE 1

Resilience Index of example polybutadiene polymers

Rubber	Tan δ at 10 cpm	Tan δ at 1000 cpm	Resilience Index at 100° C
CB23	0.954	0.407	55
CB22	0.895	0.358	54
BR-60	0.749	0.350	40
BR-40	0.841	0.446	40
Taktene 8855	0.720	0.414	31
CARIFLEX BR1220	0.487	0.439	5
BUDIENE 1207G	0.825	0.388	44

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hard-

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Additionally, the unvulcanized rubber, such as polybutadiene, in golf balls prepared according to the invention typically has a Mooney viscosity of between about 40 and about 80, more preferably, between about 45 and about 60, and most preferably, between about 45 and about 55. Mooney viscosity is typically measured according to ASTM D-1646.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-2240, between about 30 and about 60 Shore D, preferably from about 35 to about 55 Shore D. The inner cover layer, if present, preferably has a material hardness from about 50 to about 75 Shore D, preferably from about 60 to about 65 Shore D.

EXAMPLES

A variety of cores were prepared according to the present invention, as well as some cores prepared using conventional materials. All cores in Table 2 were prepared to a diameter of 1.58 inches. The recipes for each core, and values measured for compression and COR are presented in Table 2 below:

TABLE 2

Golf Ball Core Properties from Various Rubber Formulations

Ingredients	Mooney viscosity @ 100° C	1	2	3	4	5
CB23	51	100				
CB22	63		100			
BR-60	60			100		
Taktene 8855	48				100	
CARIFLEX BR1220	43					100
zinc diacrylate		28	28	28	28	28
peroxide		0.53	0.53	0.53	0.53	0.53
zinc oxide		4.3	4.3	4.3	4.3	4.3
tungsten		110	110	110	110	110
Core Properties						
compression		77	75	77	76	71
COR @ 125 ft/s		0.815	0.811	0.810	0.807	0.802

ness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0° C and −50° C are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0° C. to −50° C may be used to accurately anticipate golf ball performance, preferably at temperatures between about −20° C and −50° C.

A variety of metal sulfide cis-to-trans catalysts that successfully converted a portion of the cis-polybutadiene isomer to the trans-isomer are presented in Table 3. CARIFLEX BR1220 polybutadiene (100 phr) was reacted with zinc oxide (5 phr), dicumyl peroxide (3 phr, the free radical initiator), and zinc diacrylate (25 phr), to form the reaction product as described in the present invention.

Trans-isomer conversion percentages range from below 8 percent to above 17 percent for the various catalysts that are present in amounts ranging from below 1.7 phr to above 3.7 phr. The table clearly demonstrates the effectiveness of numerous different cis-to-trans catalysts, at varying concentrations, for increasing the trans-polybutadiene content.

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Example 1

A Core Prepared from According to the Invention, Employing an Organosulfur Cis-to-trans Catalyst

A core according to the present invention was created employing an organosulfur compound as the cis-to-trans conversion catalyst. The resultant core properties clearly demonstrate the advantages of a golf ball core made according to the current invention as compared to example cores constructed with conventional technology. The components and physical characteristics are presented in Table 4.

The compressive load of cores prepared according to the invention is approximately half of the compressive load of cores constructed in accordance with U.S. Pat. Nos. 5,697,856, 5,252,652, and 4,692,497, while at the same time retaining roughly the same, and in some cases higher, COR (resilience). The core made according to the current invention has a lower compressive load (soft), yet is resilient (fast). The compressive load is greater than that of a core constructed in accordance with U.S. Pat. No. 3,239,228, but has a significantly higher COR. The core of U.S. Pat. No 3,239,228 is very soft and very slow (very low COR)

The percent change in dynamic stiffness from 0° C. to −50° C. was also measured at both the edge and center of the cores. The dynamic stiffness at both the edge and the center

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of the core of the current invention varied only slightly, less than 20 percent, over the temperature range investigated. The core made according to U.S. Pat. No. 3,239,228 varied over 230 percent, whereas the cores made according to other conventional technology, had a dynamic stiffness that varied by greater than 130 percent, and typically by as much as 150 percent, over the same temperature range.

The percent of trans-conversion was also measured at both the center and edge of the core prepared according to the current invention, and for cores prepared as disclosed in the same four patents mentioned above, allowing a trans-gradient to be calculated. The core according to the current invention had a trans-gradient of about 32 percent from edge to center. For the core prepared according to the current invention, the pre- and post-cure trans-percentages was also measured to determine the effectiveness of that process. The percentage of polybutadiene converted to the trans-isomer ranged from almost 40 percent at the center to greater than 55 percent at the edge. Two of the cores prepared according to conventional technology, U.S. Pat. Nos. 3,239,228 and 4,692,497, had a zero trans-gradient. A third core, prepared according to U.S. Pat. No. 5,697,856, had only a slight trans-gradient, less than 18 percent from edge to center. A fourth core, prepared according to U.S Pat. No 5,252,652, had a very large gradient, almost 65 percent from edge to center.

TABLE 3

Metal Sulfide Conversion Examples

CARIFLEX BR1220	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
Dicumyl peroxide	3	3	3	3	3	3	3	3	3	3	3	3	3
Zinc Diacrylate	25	25	25	25	25	25	25	25	25	25	25	25	25
Cis-to-Trans "Catalyst"													
FeS	2.87												
MnS		2.65											
TiS$_2$			1.70										
CaS				2.20									
CoS					2.77								
MoS$_2$						2.43							
WS$_2$							3.77						
Cu$_2$S								4.65					
SeS$_2$									2.19				
Y$_2$S$_3$										2.76			
ZnS											2.97		
Sb$_2$S$_3$												3.45	
Bi$_2$S$_3$													5.22
% Trans BR isomer Precure	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
% Trans BR isomer Postcure	10.5	16.1	17.0	8.3	10.3	10.1	9.2	5.8	5.2	10.2	10.1	10.7	10.5

TABLE 4

				Examples of Conventional Golf Balls			
	Examples of Golf Balls of the Invention			US #5816944			US #4971329
Chemical Constituents	#1	#2	#3	US #3239228	US #5697856	US #5252652	US #4692497
Polybutadiene (Shell, CARIFLEX BR1220)	100	100	100		N/A	N/A	N/A
Polybutadiene (Firestone, 35 NF)				100	N/A	N/A	N/A
DMDS				2.1	N/A	N/A	N/A
Carbon Black (RA)				15	N/A	N/A	N/A
Wood Flour				24	N/A	N/A	N/A
Sulfur				24	N/A	N/A	N/A
Stearic Acid				1.5	N/A	N/A	N/A
Reogen				15	N/A	N/A	N/A

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TABLE 4-continued

| | Examples of Golf Balls of the Invention | | | | Examples of Conventional Golf Balls | | |
| | | | | | US #5816944 | | US #4971329 |
Chemical Constituents	#1	#2	#3	US #3239228	US #5697856	US #5252652	US #4692497
Vanox MBPC				2	N/A	N/A	N/A
Triethanolamine				4	N/A	N/A	N/A
Zinc oxide	5	5	5	5	N/A	N/A	N/A
Dicumyl peroxide	3	1.9	2		N/A	N/A	N/A
Zinc Diacrylate	25	25	25		N/A	N/A	N/A
Cis-Trans "Catalyst"					N/A	N/A	N/A
MnS		0.82			N/A	N/A	N/A
Ditolyldisulfide	2.5		1.5		N/A	N/A	N/A
Cu₂S				1	N/A	N/A	N/A
Resultant Core Properties							
Load(lbs) @10.8% Deflection 1.580" core	165.5	191.4	191.8	61.1	325	390	480
Coefficient of Restitution @125 ft/s	0.783	0.777	0.785	0.599	0.779	0.805	0.775
Hardness Shore C							
Surface	61	76	62	35	75	80	80.5
Center	52	52	59	30	70	61	66.5
Dynamic Stiffness @ 0° C. (N/m)							
Edge*	25338	27676	28493	8312	62757	83032	72235
Center	20783	17390	27579	8361	61071	26264	50612
Dynamic Stiffness @ −50° C. (N/m)							
Edge*	30265	34523	34455	19394	92763	109053	108242
Center	23022	20603	32195	18617	89677	28808	83183
Dynamic Stiffness Ratio at −50° C./0° C.							
Edge*	119%	125%	121%	233%	148%	131%	150%
Center	111%	118%	117%	223%	147%	110%	164%
Loss Tangent 0° C.							
Edge*	0.024	0.027	0.024	0.074	0.039	0.037	0.045
Center	0.025	0.023	0.023	0.073	0.033	0.025	0.043
Loss Tangent −50° C.							
Edge*	0.098	0.084	0.097	0.183	0.142	0.119	0.099
Center	0.067	0.071	0.085	0.180	0.129	0.059	0.095
% Trans BR isomer Precure	15	15	15	50	N/A	N/A	N/A
% Trans BR isomer Postcure							
Surface	55.8	8.4	45.5	50	30.2	24.6	15
Center	37.8	4.6	25.5	50	24.7	8.5	15
% Trans Variation (Surf.-Center)/Surf.	32%	45%	44%	0%	18%	65%	0%

*Edge is measured approximately 5 mm from the exterior surface of the measured article.

Example 2

A Core Prepared from According to the Invention, Employing an Inorganic Sulfide Cis-to-trans Catalyst

A core according to the present invention was created employing an inorganic sulfide compound as the cis-to-trans conversion catalyst. The resultant core properties clearly demonstrate the advantages of a golf ball core made according to the current invention as compared to example cores constructed with conventional technology. The components and physical characteristics are presented in Table 4.

The compressive load is approximately half of the compressive load of three cores constructed in accordance with U.S. Pat. Nos. 5,697,856, 5,252,652, and 4,692,497, while at the same time retaining roughly the same, and in some cases, a higher COR (resilience). The core made according to the current invention is soft, yet resilient (fast). The compressive load is greater than a core constructed in accordance with U.S. Pat. No. 3,239,228, but has a significantly higher COR. The core of U.S. Pat. No. 3,239,228 is very soft and very slow (low COR).

The percent change in dynamic stiffness from 0° C. to −50° C. was also measured at both the edge and center of the cores. The dynamic stiffness at both the edge and the center of the core of the current invention varied only slightly, less than 125 percent, over the temperature range investigated. The core made according to U.S. Pat. No 3,239,228 varied over 230 percent, whereas the cores made according to other conventional technology, had a dynamic stiffness that varied by greater than 130 percent, and typically by as much as 150 percent, over the same temperature range.

The percent of trans-conversion was also measured at both the center and edge of the core prepared according to the current invention, and for cores prepared according to the same four patents mentioned above, allowing a trans-gradient to be calculated. The core according to the current invention had a trans-gradient of about 45 percent from edge to center. Two of the cores prepared in accordance with U.S. Pat. Nos. 3,239,228 and 4,692,497 had a zero trans-gradient. A third core, prepared in accordance with U.S. Pat. No. 5,697,856, had only a slight trans-gradient, less than 18 percent from edge to center. A fourth core, prepared in accordance with U.S. Pat. No. 5,252,652, had a very large gradient, almost 65 percent, from edge to center.

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Example 3

A Core Prepared from According to the Invention, Employing a Blend of Organosulfur and Inorganic Sulfide Cis-to-trans Catalyst

A core according to the present invention was created employing a blend of organosulfur and inorganic sulfide compounds as the cis-to-trans conversion catalyst. The resultant core properties clearly demonstrate the advantages of a golf ball core made according to the current invention as compared to example cores constructed with conventional technology. The components and physical characteristics are presented in Table 4.

The compressive load is approximately half of the compressive load of three cores constructed in accordance with U.S. Pat. Nos. 5,697,856, 5,252,652, and 4,692,497, while at the same time retaining roughly the same, and in some cases a higher COR (resilience). The core made according to the current invention is soft, yet resilient (fast). The compressive load of the invention is greater than a fourth core constructed in accordance with U.S. Pat. No. 3,239,228, but has a significantly higher COR. The core constructed in accordance with U.S. Pat. No. 3,239,228 is very soft and very slow (low COR).

The percent change in dynamic stiffness from $0°$ C. to $-50°$ C. was also measured at both the edge and center of the cores. The dynamic stiffness at both the edge and the center of the core of the current invention varied only slightly, less than 121 percent, over the temperature range investigated. The core made in accordance with U.S. Pat. No. 3,239,228 varied over 230 percent, whereas the cores made according to other conventional technology had a dynamic stiffness that varied by greater than 130 percent, and typically by as much as 150 percent, over the same temperature range.

The percent of trans-conversion was also measured at both the center and edge of the core prepared according to the current invention, and for cores prepared to the same four patents mentioned above, allowing a trans-gradient to be calculated. The core according to the current invention had a trans-gradient that about 44 percent from edge to center. For the core prepared according to the current invention, the pre- and post-cure trans-percentages was also measured to determine the effectiveness of that process. The percentage of polybutadiene converted to the trans-isomer ranged from almost 26 percent at the center to greater than 45 percent at the edge. Two of the cores prepared in accordance with U.S. Pat. Nos. 3,239,228 and 4,692,497 had a zero trans-gradient. A third core prepared in accordance with U.S. Pat. No. 5,697,856 had only a slight trans-gradient, less than 18 percent from edge to center. A fourth core, prepared in accordance with U.S. Pat. No. 5,252,652 had a very large gradient, almost 65 percent from edge to center.

Example 4

Comparison of a Conventional Dual Core Ball to Dual Core Ball Prepared According to the Invention

A dual core golf ball according to the present invention was created having a solid center, an intermediate layer surrounding the solid center, and a multilayer cover disposed concentrically around the intermediate layer. The components and physical characteristics are presented below in Table 5.

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TABLE 5

Center Composition	Example 4: Dual Core
CARIFLEX BR1220	100
zinc diacrylate	20
dicumyl peroxide	2.5
zinc oxide	39
DTDS	0.75
Center Properties	
% trans Precure	1.5
% trans Postcure	40
load in lbs required (10.8% deflection)	109
Mantle Composition	
CB23	80
zinc diacrylate	38
VAROX 231 X1	0.42
DBDB-60	0.15
zinc oxide	6
polyisoprene	20
Inner Cover Composition and Properties	
Na SURLYN	50
Li SURLYN	50
Shore D hardness	68
thickness	0.03 in
Outer Cover Composition and Properties	
MDI polyurethane	
thickness	0.03 in

A solid center was constructed for the ball of the present invention. The center was created from CARIFLEX BR-1220 polybutadiene as the starting material, the only difference being replacing the VAROX 802-40KE-HP peroxide (conventional technology) with a DTDS cis-to-trans catalyst of the current invention and dicumyl peroxide. This substitution allows a portion of the polybutadiene material to be converted to the trans-configuration during the molding process. The resulting solid center had an outside diameter of approximately 1.15 inches. The polybutadiene reaction product prepared thereby had a trans-isomer content of 40 percent compared to the 1.5 percent trans-isomer of conventional balls. An intermediate layer, having outside diameter of approximately 1.56 inches, was constructed around the solid center to form a core. The outer layer is made of CB23 having a molecular weight of about 360,000 and a Mooney viscosity of about 51.

Examples 5–8

Comparison of Conventional Golf Balls with Those Prepared According to the Invention

A polybutadiene reaction product was prepared for two conventional prior art compositions (Examples 5–6) as well as one prepared according to the invention (Examples 7–8). The recipes for each composition can be seen in Table 6 below.

TABLE 6

	Example 5 (phr)	Example 6 (phr)	Example 7 (phr)	Example 8 (phr)
Reaction Product				
CARIFLEX BR1220	100	100	100	100
zinc oxide	26.6	2.67	26.6	26.6
barium sulfate	—	31	—	—
zinc diacrylate	20	22.3	20	20

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TABLE 6-continued

	Example 5 (phr)	Example 6 (phr)	Example 7 (phr)	Example 8 (phr)
dicumyl peroxide	2	—	2	2
VAROX 802 40KE-HP[a]	—	0.89	—	—
polymeric sulfur	0	0	0.25	0
elemental sulfur	0	0	0	0.25
pre-cure trans-polybutadiene content	1.5%	1.5%	1.5%	1.5%
Golf Ball Core				
post-cure trans-polybutadiene content in reaction product	1.5%	1.5%	12%	12%
Atti Compression	53	23	26	21
COR	n/a[b]	0.72	0.77	0.76

[a]A di-(2-t-butylisopropylperoxy)-benzene peroxide commercially available from R. T. Vanderbilt of Norwalk, CT.
[b]The core of Example 5 was sufficiently rigid to crack during testing of the coefficient of restitution, indicating an undesirably low COR.

These constituents were mixed and molded, thereby converting a percentage of cis- to a trans-conformation, in a solid sphere sized like the core of a golf ball. Examples 7–8 illustrate the significant conversion of cis-polybutadiene to trans-polybutadiene when a sulfur cis-to-trans catalyst is present according to the invention compared to the lack of conversion in Examples 5–6 when no sulfur catalyst is present. Moreover, Examples 7–8 illustrate the improved coefficient of restitution with no significant change in compression that can be achieved with golf balls including the reaction product according to the invention.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising:
a center comprising a material formed from the conversion reaction of at least a cis-to-trans catalyst and a polybutadiene, wherein the material has a molecular weight of greater than about 200,000 and a resilience index of at least about 40;
an inner cover layer; and
an outer cover layer disposed about the inner cover layer comprising a polyurethane composition.

2. The golf ball of claim 1, wherein the inner cover layer comprises at least one of an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer, or blends thereof.

3. The golf ball of claim 1, wherein the resilience index of the material is at least about 50.

4. The golf ball of claim 1, wherein the cis-to-trans catalyst comprises at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound.

5. The golf ball of claim 1, wherein the polyurethane composition comprises at least one isocyanate, at least one polyol, and at least one curing agent.

6. The golf ball of claim 1, wherein the outer cover layer has a thickness of about 0.02 inches to about 0.04 inches.

7. The golf ball of claim 1, wherein the inner cover layer has an outer diameter of about 1.55 inches or greater.

8. A golf ball comprising:
a center formed of a reaction product comprising polybutadiene and a cis-to-trans catalyst, wherein the reaction product has a molecular weight of greater than about 200,000, and wherein the reaction product comprises greater than about 32 percent trans-isomer;
an inner cover layer
an outer cover layer disposed around the inner cover layer, wherein the outer cover layer comprises a castable reactive liquid material.

9. The golf ball of claim 8, wherein the inner cover layer comprises an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer, or blends thereof.

10. The golf ball of claim 8, wherein the inner cover layer comprises a copolymer of ethylene and an unsaturated monocarboxylic acid, wherein the monocarboxylic acid is at least partially neutralized.

11. The golf ball of claim 10, wherein the monocarboxylic acid is fully neutralized.

12. The golf ball of claim 8, wherein the outer cover layer has a thickness of about 0.02 inches to about 0.04 inches and the inner cover layer has an outer diameter of about 1.55 inches or greater.

13. The golf ball of claim 8, wherein the castable reactive material comprises a prepolymer having less than about 14 percent unreacted isocyanate groups, and wherein the prepolymer is cured with a polyol, polyamine, or a mixture thereof.

14. The golf ball of claim 8, wherein the cis-to-trans catalyst comprises at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound.

15. The golf ball of claim 8, wherein the reaction product has a molecular weight of about 300,000 or greater.

16. A golf ball comprising:
a center comprising a material formed from the conversion reaction of at least a cis-to-trans catalyst and a polybutadiene, wherein the material has a molecular weight of greater than about 200,000 and a resilience index of at least about 40;
an inner cover layer; and
an outer cover layer disposed about the inner cover layer comprising a castable reactive liquid material.

17. The golf ball of claim 16, wherein the cis-to-trans catalyst comprises an organosulfur compound.

18. The golf ball of claim 17, wherein the cis-to-trans catalyst is present in an amount sufficient to result in the material comprising greater than 32 percent trans-polybutadiene isomer.

19. A golf ball of claim 18, wherein the cis-to-trans catalyst is present in an amount from about 0.1 to 5 parts per hundred based on the total material.

20. The golf ball of claim 16, wherein the resilience index is at least about 50.

21. The golf ball of claim 16, wherein the inner cover layer has a hardness of about 50 to about 75 Shore D.

22. The golf ball of claim 16, wherein the castable reactive liquid material has a material hardness of about 30 Shore D to about 60 Shore D.

* * * * *

EXHIBIT W

THIS EXHIBIT HAS BEEN REDACTED IN ITS ENTIRETY

EXHIBIT X

THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY

EXHIBIT Y

United States Patent [19]

Lynch et al.

[11] Patent Number: 4,729,861

[45] Date of Patent: Mar. 8, 1988

[54] METHOD OF MAKING GOLF BALLS

[75] Inventors: Francis deS. Lynch, Mattapoisett;
John W. Jepson, Marion; Robert A.
Brown, Mattapoisett, all of Mass.

[73] Assignee: Acushnet Company, New Bedford,
Mass.

[21] Appl. No.: 713,298

[22] Filed: Mar. 18, 1985

Related U.S. Application Data

[60] Division of Ser. No. 213,056, Dec. 4, 1980, which is a
continuation of Ser. No. 91,087, Nov. 5, 1979, aban-
doned, which is a continuation of Ser. No. 920,396,
Jun. 29, 1978, abandoned, which is a continuation of
Ser. No. 816,882, Jul. 18, 1977, abandoned, which is a
continuation of Ser. No. 716,100, Aug. 20, 1976, aban-
doned, which is a continuation of Ser. No. 363,353,
May 24, 1973, abandoned, which is a continuation-in-
part of Ser. No. 236,318, Mar. 20, 1972, abandoned.

[51] Int. Cl.⁴ A63B 37/14
[52] U.S. Cl. 264/219; 156/146;
156/245; 264/239; 273/232

[58] Field of Search 156/146, 245; 273/232;
264/219, 239, 293, 299, 320, 325

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Primary Examiner—Caleb Weston
Attorney, Agent, or Firm—Lucas & Just

[57]   ABSTRACT

Dimples are arranged on the surface of a golf ball in a
manner which makes the golf ball travel further. At
least about 80% of the distances between the closest
points of the edges of adjacent dimples are less than
about 0.065 inches and at least about 55% of the dis-
tances between the closest points of the edges of adja-
cent dimples are greater than about 0.001 inches.

24 Claims, 18 Drawing Figures
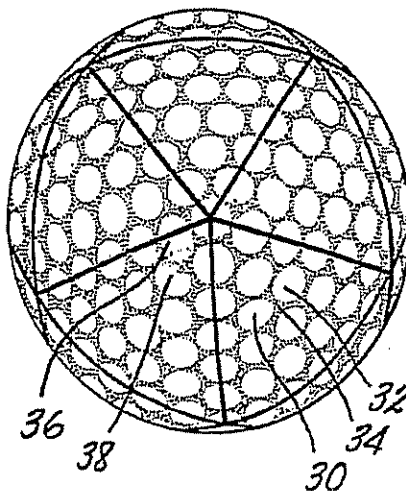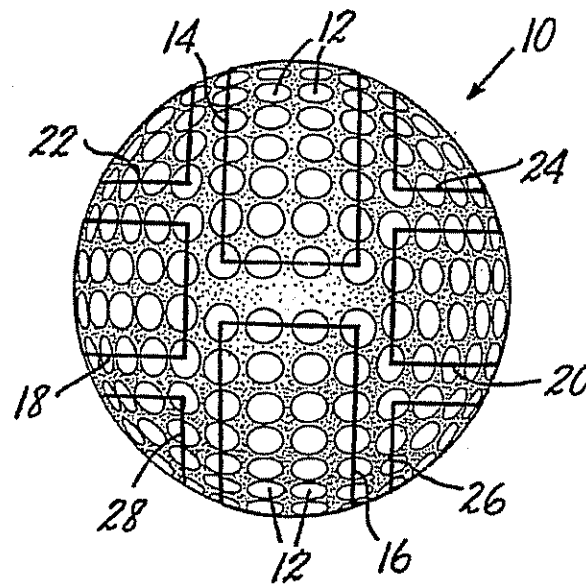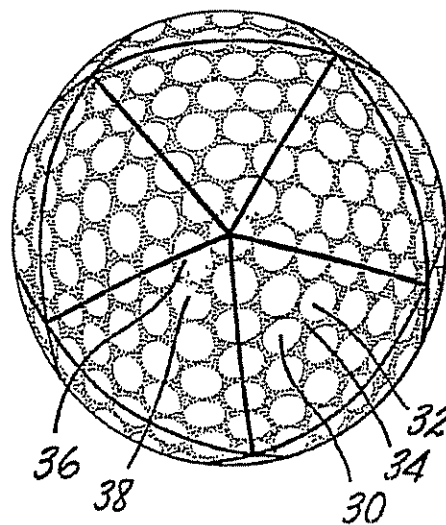
FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG. 14

FIG. 15

FIG. 16

FIG. 17

FIG. 18
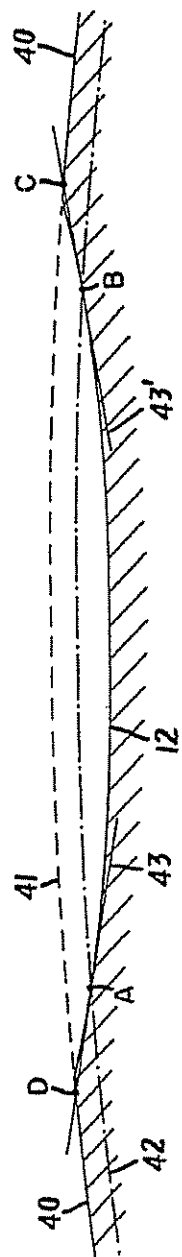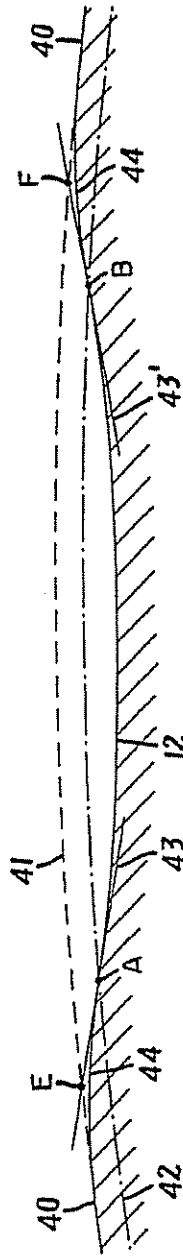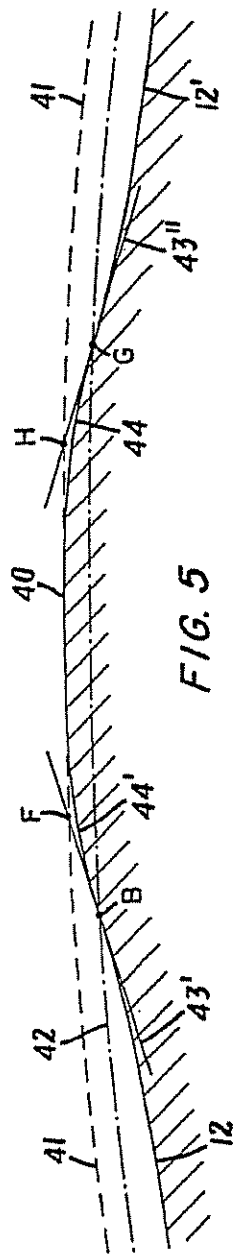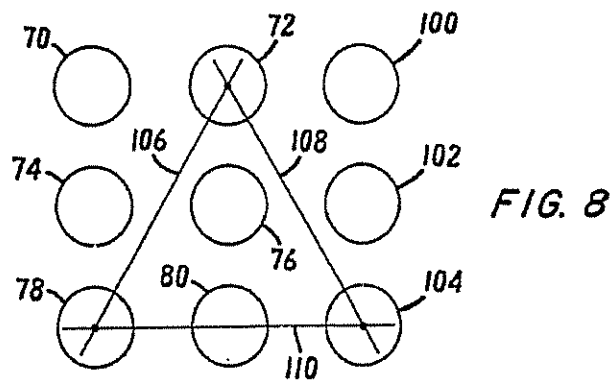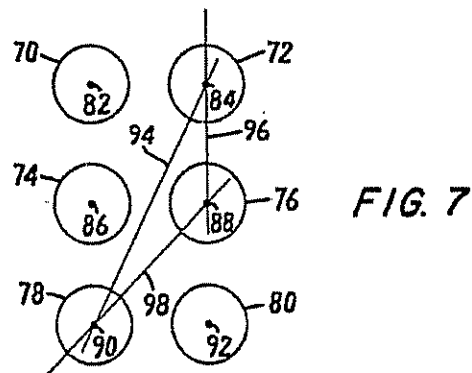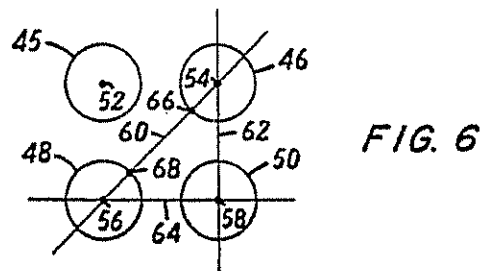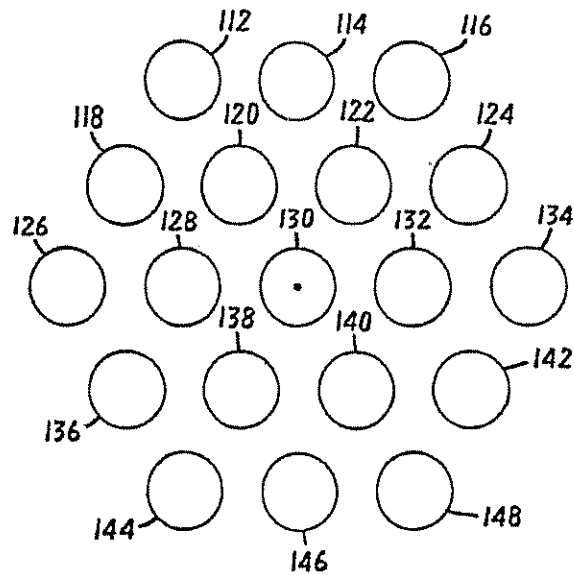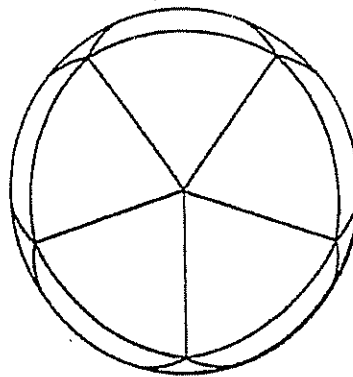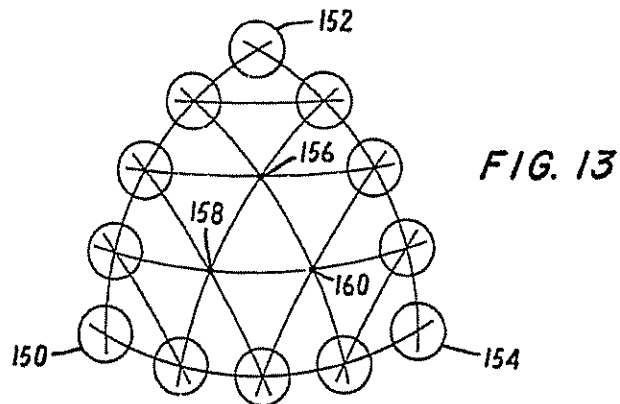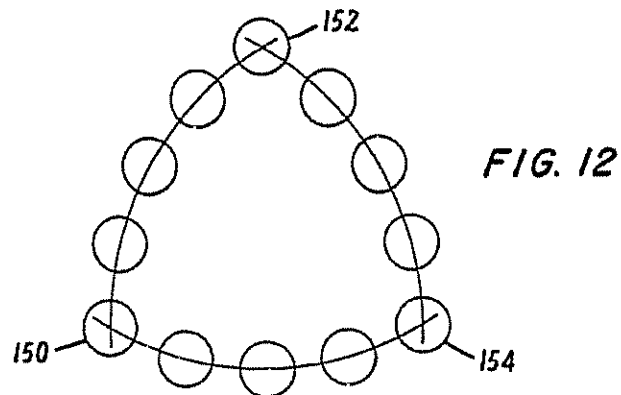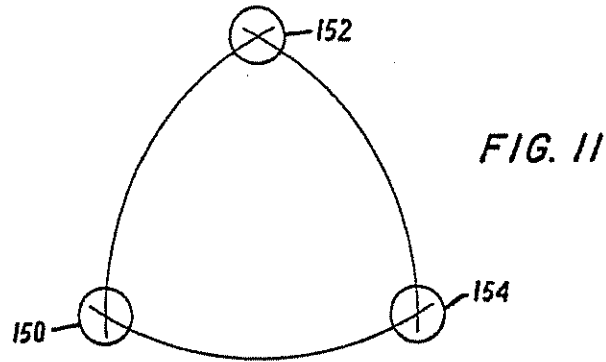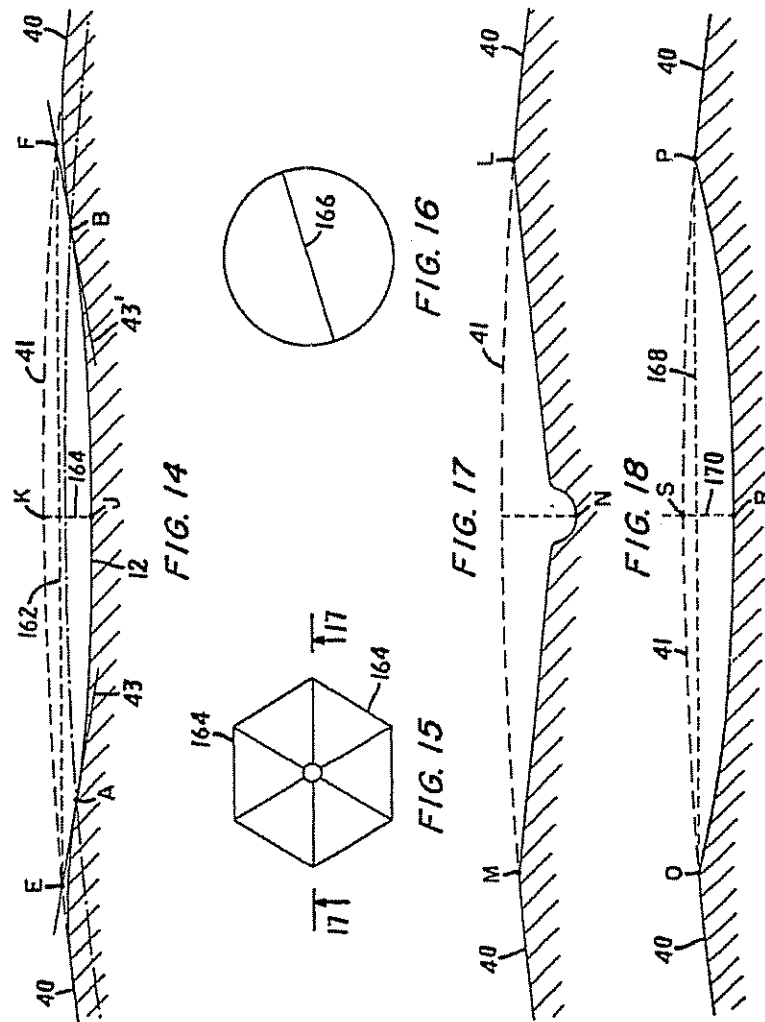
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METHOD OF MAKING GOLF BALLS

The present application is a divisional application of application Ser. No. 213,056 filed Dec. 4, 1980 which in turn was a continuation of application Ser. No. 091,087 filed Nov. 5, 1979 and now abandoned, which in turn was a continuation of application Ser. No. 920,396 filed June 29, 1978 and now abandoned, which in turn was a continuation of application Ser. No. 816,882 filed July 18, 1977 and now abandoned, which in turn was a continuation of application Ser. No. 716,100 filed Aug. 20, 1976 and now abandoned, which in turn was a continuation of application Ser. No. 363,353 filed May 24, 1973 and now abandoned, which in turn was a continuation-in-part of application Ser. No. 236,318 filed Mar. 20, 1972 and now abandoned.

The present invention relates to the spatial relationships of dimples on the surface of golf balls. By having most of the adjacent dimples no more than about 0.065 inches apart, the golf ball will travel further than a standard golf ball which is identical except for the spatial arrangement of the dimples.

For many years golf balls have had dimples on their surfaces in order to increase their aerodynamic properties whereby the ball will travel further than a smooth golf ball. By the term "dimple" it is meant an indentation in the surface of a golf ball. There have been various attempts to improve the distance obtained from a golf ball by varying the configuration of an individual dimple such as by making its diameter larger, its depth shallower, or even changing the dimple from a round to a square configuration. It has now been discovered that increased yardage can be obtained from a golf ball in which the spatial relationships of the dimples are controlled so that at least about 80% of the land distances of adjacent dimples are less than about 0.065 inches and at least about 55% of the land distances of adjacent dimples are greater than about 0.001 inches. By the term "land distance" it is intended to mean the distance between the edges of the two dimples at their closest points. The edge of the dimple is defined as the point at which the periphery of the golf ball or its continuation intersects a tangent to the sidewall of the dimple and will be hereinafter more fully explained. Since only about 55% of the land distances are greater than about 0.001 inches, it will be understood that some of the dimples may overlap. Overlapping dimples may have a negative land distance as land distance is herein defined.

It has further been discovered that when the land area between adjacent dimples is controlled within the limits as set forth in this specification, the relative size and number of the dimples is unimportant. Standard golf balls contain about 336±10 dimples on their surface. It has been found that the number of dimples on the golf ball can be varied substantially and that increased yardage will still be obtained when the limits on land distances as taught in this specification and claims are followed. It has additionally been found that the shape of the dimple is not critical. Although the preferred dimple is round, the dimple may be oval, pentagonal, hexagonal, octagonal or other shapes. In addition, more than one shape of dimple may be used on a single ball, if desired. When the term diameter is used herein, it is defined as the distance from edge to edge when the dimple is circular. When the dimple is non-circular, the term diameter is defined as the diameter of a circle which would have the same area as the area of the

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non-circular dimple. When the term depth is used herein it is defined as the distance from the continuation of the periphery line to the deepest part of a dimple which is a section of a sphere. When the dimple is not a section of a sphere, the depth in accordance with the present invention is computed by taking a cross section of the dimple at its widest point. The area of the cross section is computed and then a section of a circle of equal area is substituted for the cross section. The depth is the distance from the continuation of the periphery line to the deepest part of the section of the circle. Golf balls according to the present invention have been made with 122 dimples, 182 dimples, 252 dimples, 332 dimples and 392 dimples among others.

The critical values in accordance with the present invention are that at least about 80% of the distances between the closest points of the edges of adjacent dimples must be less than about 0.065 inches and at least about 55% of the distances between the closest points of the edges of adjacent dimples must be greater than about 0.001 inches.

There is additional advantage in controlling the depth to diameter ratio of the individual dimples. In determining the depth to diameter ratio it is necessary to include the number of dimples to be used on the ball. The basic formula for this determination is as follows:

$$S = \left[\frac{831.5(d-x) - 55.56(D-y)}{a} \right]^2 +$$

$$\left[\frac{83.15(D-y) + 555.6(d-x)}{b} \right]^2$$

wherein:
  d=average depth of all dimples in inches
  D=average diameter of all dimples in inches
  S=computed unknown (1.0 or less for present invention)

In accordance with the present invention, the computed unknown, S, will always be 1.0 or less. S can be equal to 0 but it will otherwise always be a positive number.

For a golf ball having from about 182 to about 332 dimples, the values of x, y, a, and b in accordance with the present invention will be:

$$y = 0.323 - 0.086N + 0.0122N^2$$

$$x = 0.0186 - 0.00406N + 0.000550N^2$$

$$a = 6.30 - 3.30N + 0.693N^2$$

$$b = 3.11 - 1.03N + 0.155N^2$$

N=the exact number of dimples divided by 100
This is designated as Formula 1.

For a golf ball having from 333 to about 392 dimples the same basic formula is used with the following x, y, a, and b values:

$$y = 0.287 - 0.0383N$$

$$x = 0.0162 - 0.00150N$$

$$a = 4.66 - 0.500N$$

$$b = 5.00 - 1.08N$$

N=the exact number of dimples divided by 100

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This is designated as Formula 2. Again, when S is equal to or less than 1 the depth to diameter relationship is in accordance with the present invention.

For golf balls having from 182 to 332 dimples, even better results are obtained with the basic formula when:

$$y=0.323-0.0896N+0.122N^2$$

$$x=0.0186-0.00406N+0.000550N^2$$

$$a=4.54-2.78N+0.674N^2$$

$$b=3.09-1.97N+0.412N^2$$

N=the exact number of dimples by 100
This is designated as Formula 3. It is to be pointed out that all golf balls included in Formula 3 are also included in Formula 1.

For golf balls having from 333 to 392 dimples, even better results are obtained with the basic formula when:

$$y=0.240-0.0242N$$

$$x=0.0225-0.00340N$$

$$a=13.6-3.28N$$

$$b=5.25-1.25N$$

N=the exact number of dimples divided by 100
This is designated as Formula 4. It is to be pointed out that all golf balls included in Formula 44 are also included in Formula 2.

It will be understood that there is not a sharp break between 332 and 333 dimples and that, in fact, the formulas given hereinbefore overlap in this general area. Different sets of formulas have been given for 182–332 and 333–392 dimpled balls only for the purpose of simplication since a single set of formulas for all balls would be unduly complicated. However, no matter which set of formulas is used, best results are obtained when the golf ball has from about 315 to about 340 dimples and the following values are employed in the basic formula:

x=0.0117
y=0.156
a=1.1
b=0.55

This is designated as Formula 5. Golf balls which are within this best results formula will also be included within Formulas 2 and 4 and thus necessarily within Formulas 1 and 3.

The preferred method of applying the formulas is to plot a graph of d vs. D vs. N, holding S at 1. (For Formula 5, since there is no "N" in the formula the graph will simply be a plot of d vs. D holding S at 1). The plotting of this graph is well within the skill of the art. Once the graph has been plotted, selection of one of the variables on the graph will automatically yield the other two variables.

An alternative method of applying the formulas is to first select the number of dimples to be used and then arbitrarily select a diameter and depth. If when these numbers are inserted in the appropriate formula S=1 or less, then the depth and diameter are in accordance with the present invention. For Formula 5, the depths and diameters can be the same whether the number of dimples is about 315 or about 340 or any number therebetween.

The following will serve as illustrative examples of selecting diameter and depth according to the present

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invention. Of course, the dimples were positioned on the ball in accordance with the present invention.

EXAMPLE 1

In this case it was decided to have 252 dimples which comes within Formula 1. The diameter was selected as 0.175 inches and the depth as 0.0145 inches. These values were substituted into Formula 1 and S computed as about 1.9. Since S is greater than 1.0, the depth to diameter relationship is not in accordance with the present invention.

EXAMPLE 2

Example 1 was repeated holding the dimple number at 252 and the diameter at 0.175 inches. In this case, however, the depth of the dimple were decreased to 0.0135 inches. When these values were substituted into Formula 1, S equalled about 0.7 which is less than 1.0 and thus the depth to diameter relationship was in accordance with the present invention. These distances are shown on FIG. 2 since they are within the present invention.

EXAMPLE 3

Example 2 was repeated using the same values i.e., 252 dimples, diameter of 0.175 inches and depth of 0.0135 inches. In this case, however, the values were substituted into Formula 3 to find out whether or not these values give "better" results. S was computed to be about 2.3 which is greater than 1.0 thereby indicating that these values, while within the present invention, do not give "better" results.

EXAMPLE 4

Example 3 was repeated holding the dimple number at 252 and the diameter at 0.175 inches but in this case the depth of the dimple was decreased to 0.0125 inches. When these values were substituted into Formula 3, S equalled about 0.4 which is less than 1.0 thereby indicating that these values give "better" results.

EXAMPLE 5

In this case it was decided to use 392 dimples, which comes within Formula 2. The diameter was selected as 0.130 inches and the depth as 0.009 inches. When these values were substituted into Formula 2, S was found to be about 3.0. Since S is greater than 1, the depth and diameter are not in the proper ratio in accordance with the present invention.

EXAMPLE 6

Example 5 was repeated holding the number of dimples at 392 and the depth at 0.009 inches. However, the diameter was increased to 0.140 inches. In this case S is 0.6 which is less than 1.0 and thus the depth to diameter relationship is within the limits of the present invention.

EXAMPLE 7

When Example 6 was repeated using the same values, i.e., 392 dimples, depth of 0.009 inches and diameter of 0.140 inches, but using Formula 4, S was computed to be 2.3 Since Formula 4 is the formula to be used to obtain "better" results and since the values of this example give a value greater than 1.0 in Formula 4, it is seen that these values, while within the present invention, do not give "better" results.

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EXAMPLE 8

Example 7 was repeated holding the dimple number at 392 and the depth at 0.009 inches but in this case the diameter was increased to 0.145 inches. When these values were substituted in Formula 4, S was found to be 0.1. Since S is less than 1.0, these values give "better" results.

EXAMPLE 9

In this case it was decided to have 315 dimples which comes within the best results formula i.e., Formula 5. The diameter was selected as 0.150 inches and the depth as 0.0125 inches. These values were substituted into Formula 5 and S computed as about 0.8. Since S was less than 1.0, the depth to diameter relationship is within the "rest results" of the present invention.

EXAMPLE 10

Example 9 was repeated using the same depth and diameter i.e., 0.150 inches and 0.0125 inches but in this case the golf ball had 340 dimples. Again, the S value equalled 0.8 and thus the ball was within the "best results" region of the present invention.

These and other aspects of the present invention may be more fully understood with reference to the following drawings in which:

FIG. 1 is the top half of a golf ball with dimples arranged as in today's standard golf ball;

FIG. 2 is the top half of a golf ball showing dimples in accordance with the present invention;

FIGS. 3–5 are cross sections of dimples showing the method of determining the edge of the dimple;

FIGS. 6–9 show a series of dimples and illustrate what is an "adjacent" dimple;

FIGS. 10–13 show one suitable method of arranging the dimples on the surface of the golf ball;

FIG. 14 shows the method of measuring the depth and diameter of a spherically shaped dimple;

FIGS. 15 and 16 show the method of computing the diameter of an irregularly shaped dimple; and

FIGS. 17 and 18 show the method of computing the depth of an irregularly shaped dimple.

Referring now to FIG. 1, there is seen a golf ball partially in section with dimples arranged in the manner customarily employed today. Virtually, all golf balls on the market today have dimples arranged in accordance with this pattern. For each hemisphere of the golf ball 10, the dimples 12 are arranged in two large rectangles 14 and 16, two small rectangles 18 and 20, and four triangles 22, 24, 26, and 28. Because of molding techniques, the opposite side of the golf ball virtually always has the same dimple pattern. It has been found that more than 33% of the land areas of adjacent dimples are more than 0.065 inches apart in this golf ball, even if the dimples are as large as 0.155 inches.

In FIG. 2 there is shown a golf ball made in accordance with the present invention. As indicated on the drawing, at least about 80% of the land areas of adjacent dimples are no greater than about 0.065 inches and no more than about 55% of the land areas of adjacent dimples are less than about 0.001 inches. As can be seen with reference to dimples 30 and 32, the distance 34 between the closest points of these two dimples may be more than 0.065 inches. It is only necessary that the distance between adjacent dimples be less than 0.065 inches for at least about 80% of such distances. Similarly, as can be seen with reference to dimples 36 and 38,

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there is a negative distance between the edges of the dimple since the edges overlap. In accordance with the present invention it is only necessary that at least about 55% of the distances between dimples at their closest points be greater than 0.001 inches. However, where the dimples overlap, the negative distance should in most cases be no greater than about 0.02 inches. The size of the dimples is relatively unimportant and can be varied within the diameters and depths as given hereinbefore. Different size dimples may be used on the same golf ball, if desired, provided that the critical distances between the edges of adjacent dimples at their closest points is maintained within the values as set forth herein.

Referring to FIGS. 3–5, there is seen the method of determining the point which comprises the edge of the dimple. The edge of the dimple is defined as that point at which the periphery of the golf ball or its continuation intersects a tangent to the sidewall of the dimple, said tangent being at a point about 0.003 inches from the periphery of the ball or its continuation.

In FIG. 3 is seen in cross section a golf ball having periphery 40 and continuation thereof 41 and dimple 12. The periphery and its continuation are a substantially smooth section of a sphere. Arc 42 is about 0.003 inches below curve 40-41-40 and intersects the dimple 12 at points A and B. Tangents 43 and 43' are tangent to the dimple 12 at points A and B respectively and intersect periphery 40 at points C and D respectively. Points C and D are the edges of the dimple.

In FIG. 4 is seen a golf ball with dimple 12 which has a rounded top 44. The dimple, in three dimensions, is a section of a sphere. Arc 42 is about 0.003 inches below curve 40-41-40 and intersects dimple 12 at points A and B. Tangents 43 and 43' are tangent to the dimple 12 at points A and B respectively and intersect periphery continuation 41 at points E and F respectively. Points E and F are the edges of the dimple.

Turning now to FIG. 5 there is shown a golf ball in cross section having dimples 12 and 12' partially shown with rounded tops 44 and 44'. Arc 42 is about 0.003 inches below curve 41-40-41 and intersects dimples 12 and 12' at points B and G respectively. Tangent 43' and 43" are tangent to the dimples 12 and 12' at points B and G respectively. Tangents 43' and 43" intersect periphery continuation 41 at points F and H respectively. Points F and H are the edges of dimples 12 and 12" respectively. The "land distance" between dimples 12 and 12' is measured along curve 41-40-41 from point F to point H.

Referring to FIGS. 6–9 there is seen the method of determining what is an "adjacent" dimple. An adjacent dimple is defined as one in which a triangle constructed of lines passing through the center points of 3 dimples has no included angle less than about 30°, and has no part of another dimple included therein.

Turning now to FIG. 6 there are shown 4 dimples, 45, 46, 48 and 50, having centers 52, 54, 56, and 58 respectively. If the center point of dimples 46, 48 and 50 are joined by lines, a triangle is formed having sides 60, 62, and 64 as shown. As can be seen, each of the included angles in this triangle is greater than about 30° and no part of another dimple is included within the triangle. Therefore, dimple 46 is adjacent to dimple 48, dimple 46 is adjacent to dimple 50, and dimple 48 is adjacent to dimple 50. Since in accordance with the present invention all dimples are circular or are converted to the circular, the closest points between the

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two dimples on the edges of the dimple will fall on the line which passes through the center of the two adjacent dimples. The closest points at the edges between dimples 46 and 48 are edge points 66 and 68, and therefore, the critical land distance as described hereinbefore is measured between points 66 and 68 for these adjacent dimples.

In FIG. 7 is shown a set of dimples 70, 72, 74, 76, 78, and 80, having centers 82, 84, 86, 88, 90, and 92, respectively. As shown with reference to FIG. 6, dimples 76 and 78 are "adjacent." If a triangle is formed by drawing lines through the center points of dimples 72, 78, and 76, it is seen that dimples 72 and 78 are not adjacent since the included angles formed by lines 94, 96, and by lines 94, 98 are less than 30°.

Referring to FIG. 8, there is again shown dimples 70, 72, 74, 76, 78, and 80, as well as dimples 100, 102 and 104. Lines 106, 108, and 110 form a triangle, passing through the centers of dimples 72, 78 and 104. Each of the included angles of this triangle is greater than 30°. However, dimple 72 is not adjacent to dimple 78 since at least a part of another dimple is included within the triangle. In this case, the entire dimple 76 is included within the triangle and half of the dimple 80 is included within the triangle.

In FIG. 9 is shown a series of dimples 112, 114, 116, 118, 120, 122, 124, 126, 128, 130, 132, 134, 136, 138, 140, 142, 144, 146, and 148. Referring to dimple 130, dimples 120, 122, 128, 132, 138, and 140 are adjacent thereto since a triangle can be formed with lines passing through the center points of each of these dimples without including at least a portion of another dimple and each included angle of the said triangles will be greater than about 30°. None of the dimples 112, 114, 116, 118, 124, 126, 134, 136, 142, 144, 146, or 148 are adjacent to dimple 130 since no triangle can be drawn through the center point of three dimples including one of these dimples and dimple 130 which will not include at least a section of another dimple and which will have no angle of the triangle less than about 30°.

With further reference to FIG. 9, it will be understood that for dimple 122, adjacent dimples are 114, 116, 120, 124, 130 and 132. With reference to the dimple 140, the adjacent dimples are 130, 132, 138, 142, 146, and 148 and so forth with respect to each of the dimples. For determining the critical values of having at least about 80% of the dimples being no further apart than about 0.065 inches and at least about 55% of the dimples being no closer than about 0.001 inches, the distance between each dimple and each of its adjacent dimples is measured. However, duplicate measurements are not included. Thus, with respect to dimple 130, the distance between it and dimples 120, 122, 128, 132, 138, and 140, are included, but thereafter with respect to the dimple 122, the distance between it and dimple 130 would not be included since this has already been included with respect to dimple 130.

Maximum benefit is obtained when 100% of adjacent dimples have a distance between them at their closest points of less than about 0.065 inches and when 100% of the minimum distances between the closest points of adjacent dimples are greater than about 0.001 inches.

The mechanics of positioning the dimples on the golf ball is not our invention. One suitable method is to first determine the diameter of the dimple to be used. The diameter of the dimple is preferably within the range of about 0.125 inches to about 0.245 inches. The golf ball surface is then broken down into an icosahedron which,

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in effect, triangulates the surface of the golf ball as shown partially in FIG. 10. Each of the "triangles" of the icosahedron is equilateral as shown in FIG. 11. Vertex dimples 150, 152, and 154 are situated on each of the vertices of the triangle as shown with the center of the dimple being at the vertex of each angle. Additional dimples are then situated on the sides of the "triangle." The positioning of their centers is determined by the diameter of the dimple and the "land distance" between adjacent dimples which is held within the limits as previously given. The additional dimples on the sides of the "triangle" are shown in FIG. 12. Great circles are then made between dimples which are about equidistance from the vertex dimples connecting all of the center points of the dimples on the sides of the "triangle." Additional dimples are placed where these great circles intersect. As shown in FIG. 13, these great circles intersect at points 156, 158, and 160. These points are the center points for additional dimples. This procedure is then followed with respect to each of the other "triangles" of the icosahedron. Naturally, a dimple at the vertex of three contiguous "triangles" will be a vertex dimple for each of the three triangles. It will be understood that the number of dimples on the sides of the "triangle" will vary inversely with the diameter of the dimple. According to the number of dimples on the sides of the "triangle," the number of great circles will also vary and therefore the number of dimples within the "triangle" will also vary since an additional dimple is placed wherever the great circles intersect.

The above method is only illustrative and need not be adhered too rigidly and the dimples need not be evenly spaced so long as the spacing of the dimples is within the critical limitations as hereinbefore given. Golf balls are usually made with two mold "halves" and it is convenient to adjust the dimples in the vicinity of the mold line so that no dimples fall on the partition line of the molds. In this manner, there is less difficulty in removing any "flash" from a dimple.

In FIG. 14 is shown the method of measuring the depth and diameter of a spherically shaped dimple. The dimple in this case is shown in cross section and is the same dimple as shown in FIG. 4. The diameter is measured from the edges of the dimples, points E and F, along line 162 which is a straight line. Point J is the deepest part of the dimple 12. The depth is measured from point K on the continuation of the periphery 41 to point J and is indicated by line 164. Line 164 is perpendicular to line 162.

In FIGS. 15 and 16 is shown the method of computing the diameter of an irregularly shaped dimple. FIG. 15 shows the top of a hexagonally shaped dimple as one looks directly at it and all six sides 164 are shown at the edges of the dimple. The area of the hexagonally shaped dimple is approximately 0.01765 square inches. FIG. 16 is a circle which has an equivalent area to the hexagonal area of FIG. 15 i.e, the area of the circle of FIG. 16 is 0.01765 square inches. The diameter of FIG. 16 is shown as 166 and this diameter is approximately 0.150 inches. Thus, in accordance with the present invention, the diameter of the hexagonally shaped dimple of FIG. 15 is 0.150 inches. It is important to note that the diameter of an irregularly shaped dimple is not measured directly on the irregularly shaped dimple but is always a diameter of a circle which has an area equivalent to that of the irregularly shaped dimple.

In like manner, the depth of an irregularly shaped dimple is computed on the basis of a spherically shaped

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dimple. In FIG. 17 is shown a cross section of an irregularly shaped dimple which in this case is the same dimple as is shown in FIG. 15. For purposes of determining the depth of the dimple, the cross section is always taken across the widest part of the dimple which passes through the deepest part of the dimple. The edge of the dimple is shown at points L and M and was determined in accordance with the present invention as set out in FIGS. 3 and 4. The periphery is shown at 41 and the deepest point of the dimple is shown at point N. The area of the cross section of the dimple up to the continuation of the periphery (as shown, enclosed by lines M,N, N,L, and L,M along line 41) is computed and found to be 0.00113 square inches. The equivalent area of a section of a circle is then substituted for the dimple as shown in FIG. 18. Points O and P are the edges of the diameter of an equivalent dimple as determined in accordance with FIGS. 15 and 16 and line 168 is a straight line between lines O and P and corresponds to the diameter line 166 of FIG. 16. Point R is the deepest part of the dimple and line 170 is perpendicular to line 168. Line 170 intersects the continuation of the periphery 41 at point S and the depth as measured from point S to point R is 0.0113 inches. It is important to note that in accordance with the present invention the depth of the dimple is measured from a cross section of a circle having an equivalent area to that of a cross section of the irregularly shaped dimple rather than being measured on the actual dimple.

In all cases, measurements made in accordance with the present invention are made on a finished golf ball, since it is the final form of the golf ball which affects aerodynamic properties as opposed to some intermediate construction of the golf ball. In most cases, a finished golf ball will have one or more layers of paint affixed to the surface thereof and in these cases the measurements are made after the final coat of paint or other surface finish has been applied. With some of the new solid balls, however, a finished ball will not have any surface layer such as paint since it is not necessary. It will be understood that in these cases a finished ball means a ball that is unpainted. It will therefore be understood that the term "finished ball" can cover either a painted or an unpainted ball but in either case means the completed ball in the form in which it is intended to be sold to the consumer.

It will be understood that the claims are intended to cover all changes and modifications of the preferred embodiments of the invention, herein chosen for the purpose of illustration, which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A method of manufacturing a golf ball having dimples in the outer periphery thereof comprising the steps of:
   (A) selecting a golf ball structure onto the surface of which dimples can be molded;
   (B) determining the dimple number, dimple diameter and dimple depth by:
   (a) selecting the number of dimples to be used, the said number of dimples being between 182 and 392;
   (b) selecting a dimple diameter and dimple depth that satisfy the following relationship:

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$$S = \left[\frac{831.5(d-x) - 55.56(D-y)}{a} \right]^2 + \left[\frac{83.15(D-y) + 555.6(d-x)}{b} \right]^2$$

in which:
   S=a value of 0 to 1.0
   d=average depth of all dimples in inches
   D=average diameter of all dimples in inches
and wherein:
a value N is obtained by dividing the exact number of dimples by 100, and x, y, a and b are defined by the following relations as functions of N: when the number of dimples is between 182 and 332:

$$y = 0.323 - 0.0896N + 0.0122N^2$$

$$x = 0.0186 - 0.00406N + 0.000550N^2$$

$$a = 6.30 - 3.30N + 0.693N^2$$

$$b = 3.11 - 1.03N + 0.155N^2$$

and when the number of dimples is between 333 and 392:

$$y = 0.287 - 0.0383N$$

$$x = 0.0162 - 0.00150N$$

$$a = 4.66 - 0.500N$$

$$b = 5.00 - 1.08N$$

   (C) making golf ball molds by positioning the selected dimples on the golf ball mold so that the surface of the golf ball made therefrom will have at least 80% of the distances between the closest points of the edges of adjacent dimples less than about 0.065 inches, and at least 55% of the distances between the closest points of the edges of adjacent dimples greater than 0.001 inches the edge of the dimples being defined as the point of intersection of the periphery of the golf ball or its continuation and a tangent to the sidewall of the dimples at a point 0.003 inches below the periphery of the golf ball or its continuation;
   (D) forming the dimples on the surface of the golf ball by molding a golf ball in the mold;
   (E) removing the formed golf ball from the mold; and
   (F) finishing the golf ball.
2. The method of claim 1 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is less than 0.065 inches.
3. The method of claim 1 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distance between the edges of adjacent dimples is greater than 0.001 inches.
4. The method of claim 1 wherein the dimples are circular.
5. The method of claim 1 wherein the selected number of dimples is from 182 to 332 and x, y, a and b are defined by the following relations as functions N:

$$y = 0.323 - 0.0896N + 0.0122N^2$$

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$$x = 0.0186 - 0.00406N + 0.000550N^2$$

$$a = 4.54 - 2.78N + 0.674N^2$$

$$b = 3.09 - 1.97N + 0.412N^2.$$

6. The method of claim 5 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of the adjacent dimples is less than 0.065 inches.

7. The method of claim 6 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is greater than 0.001 inches.

8. The method of claim 6 wherein the dimples are circular.

9. The method of claim 1 wherein the selected number of dimples is from 333 to 392 and x, y, a and b are defined by the following relations as functions of N:

$$y = 0.287 - 0.0383N$$

$$x = 0.0162 - 0.00150N$$

$$a = 4.66 - 0.500N$$

$$b = 5.00 - 1.08N.$$

10. The method of claim 9 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is less than 0.0065 inches.

11. The method of claim 9 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of the adjacent dimples is greater than 0.001 inches.

12. The method of claim 9 wherein the dimples are circular.

13. The method of claim 1 wherein the selected number of dimples is from 182 to 332 and x, y, a and b are defined by the following relations as functions of N:

$$y = 0.323 - 0.0896N + 0.0122N^2$$

$$x = 0.0186 - 0.00406N + 0.000550N^2$$

$$a = 6.30 - 3.30N + 0.693N^2$$

$$b = 3.09 - 1.97N + 0.412N^2.$$

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14. The method of claim 13 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is less than 0.065 inches.

15. The method of claim 13 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is greater than 0.001 inches.

16. The method of claim 15 wherein the dimples are circular.

17. The method of claim 1 wherein the selected number of dimples is from 333 to 392 and x, y, a and b are defined by the following relations as functions of N:

$$y = 0.240 - 0.0242N$$

$$x = 0.0225 - 0.00340N$$

$$a = 13.6 - 3.28N$$

$$b = 5.25 - 1.25N.$$

18. The method of claim 17 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is less than 0.065 inches.

19. The method of claim 17 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is greater than 0.001 inches.

20. The method of claim 17 wherein the dimples are circular.

21. The method of claim 17 wherein the selected number of dimples is from 315 to 340 and x, y, a and b are as follows:

$$x = 0.0117$$
$$y = 0.156$$
$$a = 1.1$$
$$b = 0.55.$$

22. The method of claim 21 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is less than 0.065 dimples.

23. The method of claim 21 wherein the positioning of the selected dimples in the surface of the golf ball is such that 100% of the closest distances between the edges of adjacent dimples is greater than 0.001 inches.

24. The method of claim 21 wherein the dimples are circular.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,729,861

DATED   : March 8, 1988

Page 1 of 2

INVENTOR(S) : Francis deS. Lynch et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 41, delete "the" (second instance).

Column 2, line 48, change "0.086N" to --0.0896N--.

Column 3, line 14, after "dimples" insert --divided--.

Column 3, line 31, change "44" to --4--.

Column 5, line 6, change "in" to --into--.

Column 6, line 47, change "12" " to --12'--.

Column 10, line 67, after "functions" insert --of--.

Column 11, line 12, change the dependency from "claim 6" to --claim 5--.

Column 11, line 16, change the dependency from "claim 6" to --claim 5--.

Column 11, line 32, change "0.0065" to --0.065--.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,729,861   Page 2 of 2

DATED   : March 8, 1988

INVENTOR(S) : Francis deS. Lynch et al

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 12, line 9, change the dependency from "claim 15" to —claim 13—.

Signed and Sealed this

Eighteenth Day of October, 1988

Attest:

DONALD J. QUIGG

Attesting Officer   Commissioner of Patents and Trademarks

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,729,861

DATED   : March 8, 1988

INVENTOR(S) : Francis deS. Lynch et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 12, line 32, change the dependency from "claim 17"

to read — claim 1 —.

Signed and Sealed this

Thirty-first Day of January, 1989

Attest:

DONALD J. QUIGG

Attesting Officer   *Commissioner of Patents and Trademarks*

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,729,861   Page 1 of 2

DATED   : March 8, 1988

INVENTOR(S) : Francis deS. Lynch et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 4, line 17, after "dimple" change "were" to --was--;

Column 5, line 17, change "rest" to --best--;

Column 6, line 43, change "Tangent" to --Tangents--;

Column 7, line 52, change "distance" to --distances--;

Column 8, line 13, change "equidistance" to --equidistant--;

Column 10, line 61, change "distance" to --distances--;

Column 11, line 36, delete "the"; and

Column 12, line 43, after "0.065" delete "dimples" and substitute therefor --inches--.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. :   4,729,861   Page 2 of 2

DATED   :   March 8, 1988

INVENTOR(S) :   Francis deS. Lynch et al.

It is certified that error appears in the above–identified patent and that said Letters Patent is hereby corrected as shown below:

Column 11, line 50, change "$b=3.09-1.97N+0.412N^2$" to --$b=3.11-1.03N+0.155N^2$--.

Signed and Sealed this

Twenty-seventh Day of November, 1990

Attest:

HARRY F. MANBECK, JR.

Attesting Officer   *Commissioner of Patents and Trademarks*